

Environmental Characterization of Geokinetics'
In-situ Oil Shale Retorting Technology

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by

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related polluttional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

New synthetic fuel processes under development must be characterized prior to commercialization so that pollution control needs can be identified and control methods can be integrated with process designs. Shale oil recovery processes are expected to have some unique air, water, and solid waste pollution control requirements. This report presents the results of an air and water sampling and analysis research program conducted at an *in-situ* retorting facility operated by Geokinetics, Inc., in Uintah County, Utah. Studies of this nature may serve as a basis for determining additional testing needs and other efforts to define cost-effective solutions to potential pollution problems associated with shale oil production. Further information on environmental aspects of oil shale processing can be obtained from IERL-Ci.

David G. Stephan
Director
Industrial Environmental Research Laboratory, Cincinnati

ABSTRACT

The objective of this research program was to physically, chemically, and biologically characterize air emissions and water effluents from *in-situ* oil shale retorting. Geokinetics, Inc., agreed to allow Monsanto Research Corporation to sample and analyze emissions and effluents from Retort No. 17, a pilot-scale unit producing 30 barrels of crude shale oil per day and located at the "Kamp Kerogen" site in Uintah County, Utah. The potential pollution sources tested were the retort off-gases before and after mist elimination, the exhaust from thermal incineration of the demister outlet gases, fugitive gas seepage through the retort surface and around well casings, retort water after oil separation, and evaporation pond water.

The three stack gas streams were analyzed for criteria pollutants (carbon monoxide, hydrocarbons, oxides of nitrogen and sulfur, and particulate matter) as well as ammonia, arsine, hydrogen cyanide, and trace elements. Carbon monoxide, total hydrocarbons, and C₁ through C₆ hydrocarbon fractions were quantified in the fugitive emission samples. Conventional pollutants and water quality parameters, organic priority pollutants, and trace elements were measured in the samples of retort water and evaporation pond water. Selected air and water pollution samples were tested for biological activity, using the Ames mutagenicity assay, the Chinese hamster ovary (CHO) clonal toxicity assay, and the rabbit alveolar macrophage (RAM) cytotoxicity assay.

This report was submitted in partial fulfillment of Work Directive No. 13 of Contract No. 68-03-2550 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period from November 22, 1978, to December 21, 1979; work was completed as of January 18, 1980.

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SECTION 1

INTRODUCTION

Oil shale has been recognized as a potentially substantial energy resource in the United States for more than 100 years. Recently, increasing dependence on foreign oil supplies and rapidly escalating oil prices have provided new incentive for shale oil recovery from deposits in Colorado, Utah, and Wyoming. At least four domestic firms (Colony Development Operation, Paraho Development Corporation, Superior Oil Company, and Union Oil Company) have developed surface retorting processes, in which oil shale is mined and crushed prior to thermal processing in aboveground facilities. Therefore, a good deal of substantial research is currently being directed toward the development of *in-situ* or modified *in-situ* retorting processes. *In-situ* or modified *in-situ* processes, in which the shale bed is hydraulically or explosively fractured and retorting is carried out underground, are now being developed by Equity Oil Company, Geokinetics, Inc., Rio Blanco Oil Shale Company, and Occidental Oil Shale, Inc.

Despite the benefits of shale oil as an alternative energy source, air emissions, water effluents, and solid wastes could have an adverse impacts on the environment if uncontrolled. Byproduct gases released during the retorting process may contain a complex mixture of criteria pollutants (carbon monoxide, hydrocarbons, oxides of nitrogen and sulfur, and particulate matter) and other non-criteria pollutant materials, such as ammonia, hydrogen cyanide, and hydrogen sulfide, all of which could have a deleterious effect on the region's pristine air quality. Similarly, contaminated wastewaters from oil shale processing operations might degrade the existing water quality if discharged without proper treatment. Air, water, and solid waste characterization data must be obtained in order to identify suitable control strategies prior to commercialization of an oil shale industry.

In order to fill the need for preliminary data on potential environmental impacts, the Environmental Protection Agency's Industrial Environmental Research Laboratory (IERL), Cincinnati, Ohio, contracted with Monsanto Research Corporation (MRC) to study air emissions and water effluents from true *in-situ* oil shale retorting. To meet this objective, MRC obtained permission from Geokinetics, Inc., and the Department of Energy's Laramie Energy Technology Center to conduct a sampling and analysis program at Geokinetics Retort No. 17 at the "Kamp Kerogen" site in Uintah

County, Utah. This report describes the techniques employed for and the results obtained from environmental characterization of Geokinetics' horizontal *in-situ* oil shale retorting technology. A description of Geokinetics' retorting process is given in Section 3. Section 4 presents the rationale for the selection of pollution sources for testing, followed by a discussion of the sampling and analytical techniques used for testing air emissions and water effluents. Section 5 discusses the results of quantification of all environmental discharges which were studied at Geokinetics Retort No. 17.

SECTION 2

SUMMARY

Monsanto Research Corporation (MRC) conducted an environmental assessment of shale oil production operations by field sampling of Retort No. 17, operated by Geokinetics, Inc., using horizontal *in-situ* retorting technology. This pilot-scale retort, rubblized in May 1978 and ignited in April 1979, was sampled from July 16 to July 26, during which time the crude shale oil production rate was approximately 5 m³ (30 barrels) per day. The potential pollution sources selected for characterization were: raw retort off-gases before ("demister inlet") and after oil mist removal ("demister outlet"), exhaust from thermal incineration of the demister outlet gases, fugitive gas seepage through the retort surface and around well casings, retort water after oil separation, and evaporation pond water.

None of the carbon monoxide produced in Retort No. 17, and detected in both the inlet and outlet of the demister, was released to the atmosphere because of complete combustion in the process gas incinerator, which operated at 677°C. The incinerator also accomplished 97 percent destruction of the vaporous hydrocarbons in the raw retort off-gases, the residual emissions amounting to 0.6 kg/hr. The presence of residual particulate matter (0.43 kg/hr) in the incinerator exhaust indicated that some fraction of that material in the demister outlet gases may have been composed of inorganic solids, as opposed to condensed organic compounds. Nitrogen oxides (0.9 kg/hr) were formed in the incinerator via oxidation of ammonia from the demister outlet gases and reaction of nitrogen and oxygen in the combustion air. Hydrogen sulfide and other sulfur compounds generated during oil shale retorting accounted for the incinerator's sulfur oxide emissions (8.4 kg/hr). None of the three noncriteria pollutants measured (ammonia, arsine, hydrogen cyanide) was observed at significant levels in the incinerator exhaust.

Samples of the three process and stack gas streams at Geokinetics Retort No. 17 were analyzed for 29 trace elements in both the particulate matter and the gas phase. The trace elements detected in the largest quantities were: (1) demister inlet - boron, arsenic, tin, lead, and iron; (2) demister outlet - arsenic and lead; and (3) incinerator outlet - tin, lead, and arsenic.

The demister outlet gases from Retort No. 17 were sampled for biological activity using a filter to collect particulate matter and an XAD-2 resin trap for semivolatile organic compounds. As determined by the Ames assay, extracted particulate matter was the primary source of mutagenic activity in the demister outlet gases. Acetone extracts of both the filter and the resin demonstrated only low to moderate toxicity in bioassays with Chinese hamster ovary (CHO) cells and rabbit alveolar macrophages (RAM).

Fugitive hydrocarbon emission rates due to seepage through the overburden at Geokinetics Retort No. 17 ranged from 0.2 to 18 g/m²/hr, with an average of 5.5 g/m²/hr. Total fugitive hydrocarbon emissions, including leakage around well casings, were 6.0 kg/hr, calculated in part from the retort surface area of 1,043 m². Obviously, wetting and tamping of the retort surface prior to burning does not eliminate all means of fugitive gas seepage, which may amount to as much as one-third to one-half of the total volume of gas injected into the formation. Ambient hydrocarbon concentrations due to these fugitive emissions represent a potential exposure hazard only in the immediate vicinity of the retort, as is the case for carbon monoxide emissions, which were measured at rates up to 23 g/m²/hr.

As is typical of wastewaters from oil shale processing, both the retort water and evaporation pond water collected at the Geokinetics site exhibited high levels of alkalinity (16,600 and 22,400 mg/L, respectively), chemical oxygen demand (7,200 and 10,900 mg/L), and dissolved solids (9,400 and 28,400 mg/L). None of 89 organic priority pollutants was present in either water sample at a concentration greater than 1.7 mg/L (acrylonitrile in the evaporation pond). Both the retort water and the evaporation pond water contained significant amounts of several trace elements, particularly arsenic (1.6 and 15 mg/L, respectively), boron (61 and 186 mg/L), iron (0.8 and 1.6 mg/L), molybdenum (0.3 and 6.9 mg/L), and strontium (0.7 and 0.9 mg/L).

SECTION 3

RETORTING PROCESS DESCRIPTION

On July 22, 1977, Geokinetics, Inc., signed a contract with the U.S. Energy Research and Development Administration (now the Department of Energy) to develop a process for explosive fragmentation and horizontal *in-situ* retorting of oil shale deposits that are located under shallow overburden [1]. Cooperative Agreement No. ET-76-A-03-1787, valued at about \$9.2 M, was intended to improve the shale oil recovery technique developed by Geokinetics in laboratory and field work dating back to 1973 [1]. The project site, leased from the State of Utah in March 1975, is located in the northeast quadrant of Section 2, Township 14 South, Range 22 East, Uintah County [1, 2]. As of December 31, 1978, Geokinetics had blasted and burned ten retorts at the "Kamp Kerogen" site, producing over 800 m³ (5,000 bbl) of crude shale oil [2].

In the Geokinetics horizontal *in-situ* retorting process, a pattern of blastholes is drilled from the surface, through the overburden, and into the oil shale bed. The holes are loaded with explosives and then fired using a carefully planned blast system. The blast yields a well-fragmented mass of rock, with high permeability, and also a sloped-bottom bed which allows shale oil to drain to a sump for recovery by production wells; the result is shown in Figure 1 [2]. After rubblization of the shale deposit is completed, surface equipment such as that shown in Figure 2 [2], along with thermocouple and pressure wells, is installed.

The oil shale is ignited with burning charcoal at the air injection wells, which are drilled at one end of the retort. Injected air establishes and maintains a horizontally moving burn front that occupies the entire cross section of the rubblized bed.

-
- [1] Environmental Prespective on the Emerging Oil Shale Industry, 2 vols., U.S. Environmental Protection Agency, Cincinnati, Ohio, March 1980. 1,043 pp.
 - [2] Lekas, M. A. Progress Report on the Geokinetics Horizontal *In-Situ* Retorting Process. In: Twelfth Oil Shale Symposium Proceedings, Colorado School of Mines, Golden, Colorado, August 1979. pp. 228-236.

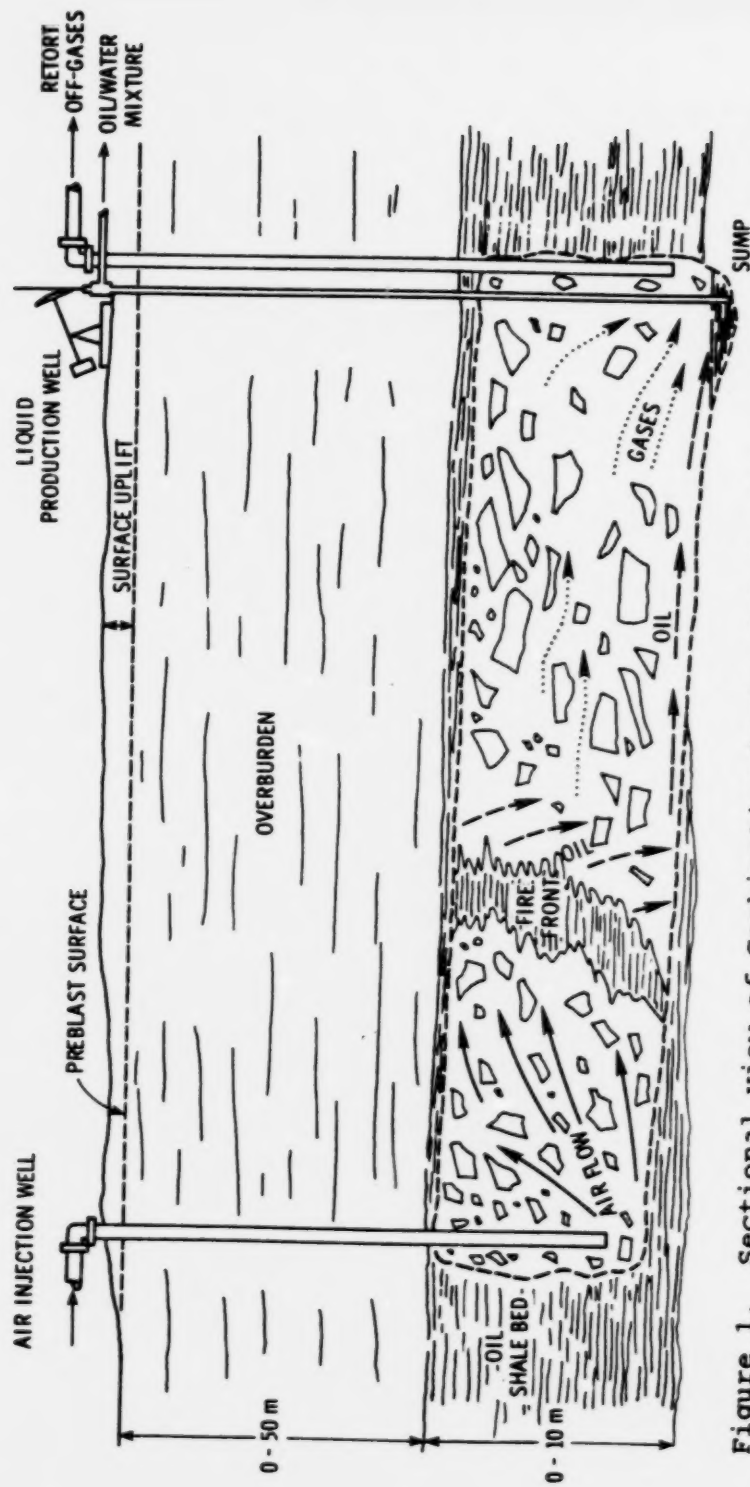


Figure 1. Sectional view of Geokinetics horizontal in-situ oil shale retort [2].

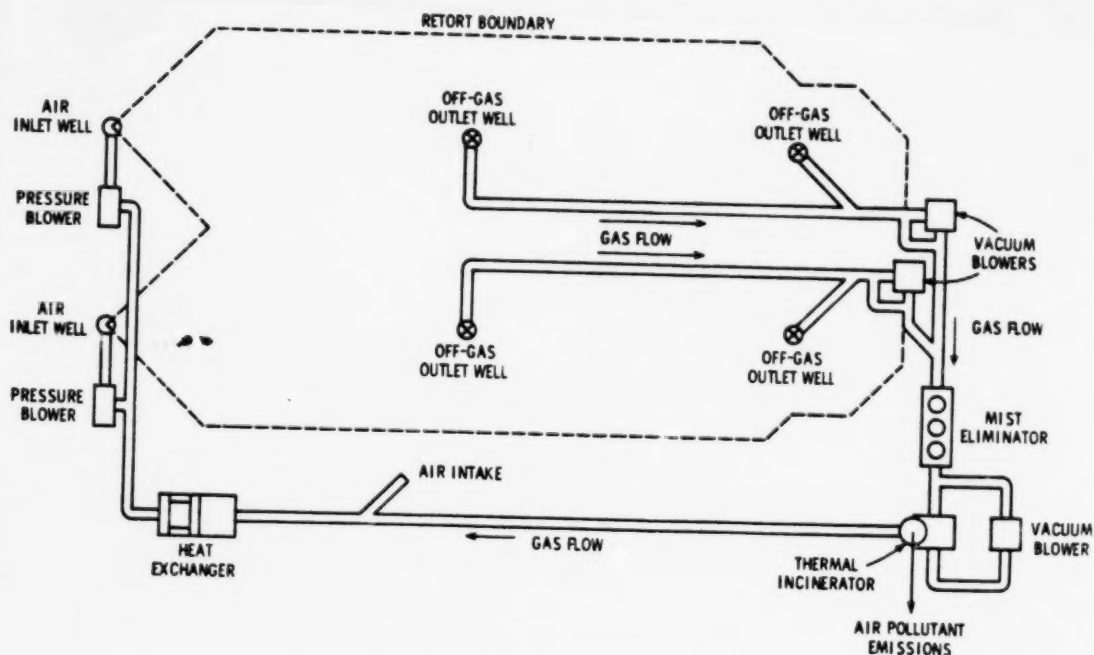


Figure 2. Overhead view of surface equipment for handling off-gases from Geokinetics Retort No. 17 [3].

Off-gases containing oil mist exit through output holes at the downstream end of the retort. These off-gases are then passed through a three-element, packed-tower mist eliminator to remove entrained oil and water, prior to combustion in a thermal incinerator. Provisions are made for firing propane as a supplemental fuel if the heat content of the demisted gases is insufficient [4].

The mixture of shale oil and water which collects in the sump is pumped by aboveground production wells to an oil-water separator tank, along with the liquid recovered in the mist eliminator described above. From the separator, the aqueous layer is sent to an evaporation pond, and the crude shale oil is pumped to product storage tanks.

[3] Geokinetics, Inc. Geokinetics Group *In-Situ* Oil Shale Recovery Project: Quarterly Report, January-March 1979. Concord, California.

[4] Geokinetics, Inc. Geokinetics Group *In-Situ* Oil Shale Recovery Project: First Annual Report. Concord, California, March 1978. 64 pp.

SECTION 4

TESTING PROGRAM AND PROCEDURES

SAMPLING AND ANALYSIS PROGRAM DESIGN

Pollution Source Selection

The principal objective of this environmental screening program was to physically, chemically, and biologically characterize emissions and effluents from *in-situ* oil shale retorting. However, these efforts were also meant to supplement, although not necessarily duplicate, ongoing environmental research studies conducted by Geokinetics, Inc., and the Department of Energy's Laramie Energy Technology Center. The potential pollution sources associated with Geokinetics' retorting technology, the testing of which was judged to best fulfill these objectives, were the off-gases before ("demister inlet") and after mist elimination ("demister outlet"), the exhaust from thermal incineration of the demister outlet gases, fugitive gas seepage through the retort overburden and around well casings, retort water after oil separation, and evaporation pond water [5].

Other pollution sources, such as groundwater contamination, volatilization from the evaporation pond, or bottoms from the separator tank, while also of potential significance, were not investigated by MRC, in order to utilize the available funding for a "wide-scan" screening study. It is also important to note that several of the sources selected for testing, namely the demister inlet and outlet and retort water, are sampled prior to treatment. Therefore, their characterization will enable the EPA to identify pollution control methods other than those implemented by Geokinetics and to estimate the environmental impacts of these treatment alternatives.

-
- [5] Delaney, J. L. Sampling and Analytical Plan for Environmental Characterization of *In-Situ* Oil Shale Retorting at Geokinetics, Inc., Kamp Kerogen, Retort 17. Contract No. 68-03-2550, U.S. Environmental Protection Agency, Cincinnati, Ohio, March 1979. 78 pp.

Test Site Selection, Preparation, and Operation

As of December 31, 1978, Geokinetics had blasted 18 retorts, and burned ten of these, at the Kamp Kerogen *in-situ* oil shale processing site in Uintah County, Utah [2]. For this sampling and analysis program, Retort No. 17 was selected for testing. This retort, blasted in May 1978, contained 11,800 Mg (13,000 tons) of broken oil shale, in a bed 5.2 m (17 ft) thick, 22.0 m (72 ft) wide, and 47.5 m (156 ft) long, situated under an average of 7.9 m (26 ft) of overburden [2]. As discussed above, gas stream samples were to be taken from the inlet and the outlet of the mist eliminator and from the thermal incinerator exhaust. During a presurvey visit conducted on February 13, 1979, it was requested that Geokinetics personnel install sampling ports at the locations indicated in Figures 3 and 4; this operation was completed in May. Additional details of all three gas stream sampling locations at Geokinetics Retort No. 17 are shown in Figures 5 and 6. The demister outlet sample ports are located at the extreme left of Figure 5, and the demister inlet sampling locations, as well as the emergency flare, can be seen at the right of that figure. The thermal incinerator used to combust the outlet gases from the mist eliminator is shown in Figure 6. The sample port and platform are located at the upper left, and a Source Assessment Sampling System (SASS) console is visible at the lower right.

Retort No. 17 was ignited in mid-April 1979. MRC personnel performed field sampling and analysis from July 16 to July 26. During that time period, the crude shale oil production rate was 5 m³ (30 bbl) per day, and the burn front advanced approximately 0.15 m (0.5 ft) per day (personal communication, S. G. Mankowski, Geokinetics, Inc., to J. L. Delaney, Monsanto Research Corporation, July 16, 1979). No supplemental fuel was fired to the process gas incinerator; a 30 kw (40 hp) vacuum blower, designed to pull 1.4 m³/s (3,000 ft³/min) of gas through the underground retort, was not operated during the sampling period.

Gas Sampling and Analysis

The selected process and stack gas streams from *in-situ* oil shale retorting contained combustion products, organic and inorganic compounds, and particulate matter. The sampling and analytical methods used for gas stream characterization are summarized in Table 1. Table 2 lists the number of tests performed for each gas stream that was sampled. In addition to the above tests, the sampling and analytical plan for this program indicated that bag samples would be collected for determination of carbon disulfide (CS₂), carbonyl sulfide (COS), and hydrogen sulfide (H₂S), and that Andersen cascade impactors would be used to determine the size distribution of the particulate matter. Neither test was possible, the former because the portable gas chromatograph with a sulfur-specific flame photometric detector would not function

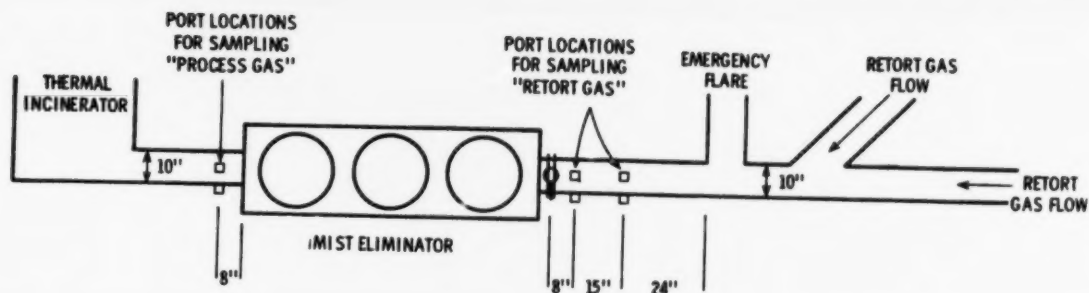


Figure 3. Port locations for sampling mist eliminator inlet and outlet gases at Geokinetics Retort No. 17.

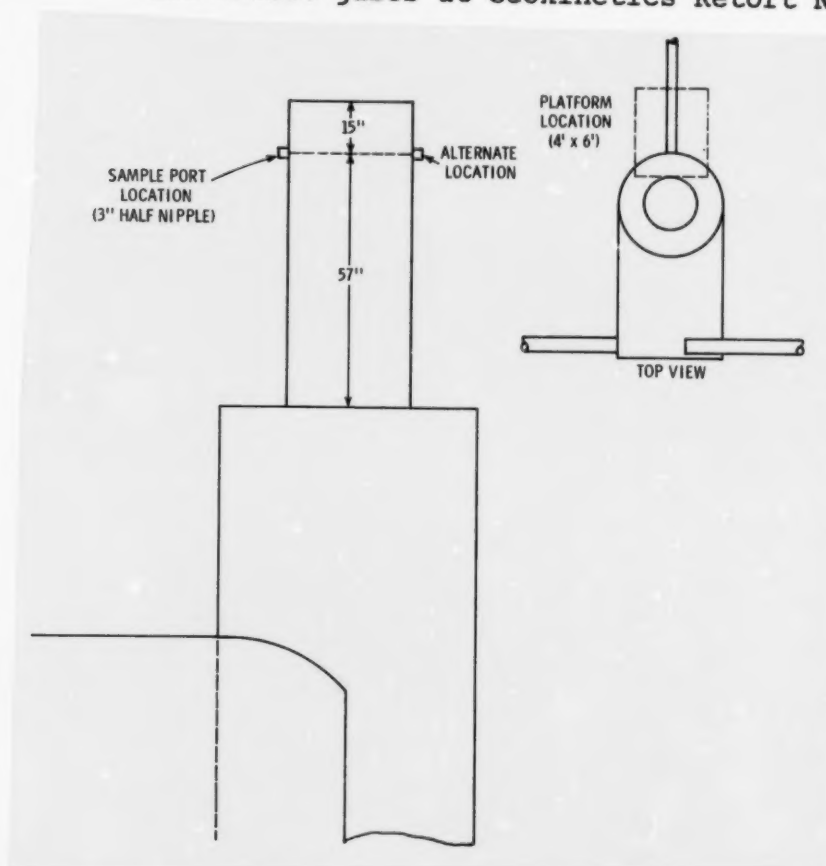


Figure 4. Sampling port and platform locations for thermal incinerator at Geokinetics Retort No. 17.

TABLE 1. SAMPLING AND ANALYSIS TECHNIQUES USED FOR CHARACTERIZATION OF GAS STREAMS FROM GEOKINETICS RETORT NO. 17

Characteristic	Sampling method	Analytical method
Particulate loading	Method 5 ^a	Gravimetric ^b
Elemental composition of particulates		AA and ICAP ^b
Moisture		Volumetric
Sulfur oxides (SO _x)	Method 6 ^a	Titration
Nitrogen oxides (NO _x)	Method 7 ^a	Colorimeter
Ammonia (NH ₃)	Impinger trains	Ion-selective electrode
Hydrogen cyanide (HCN)		Colorimeter
Arsine (AsH ₃)		AA ^b
Organics	Packed porous polymer tubes	GC/MS ^c
Total hydrocarbons		
Specific C ₁ -C ₆ hydrocarbons	Grab (bag) samples	GC/FID ^d
Specific organics		GC/MS ^c
CO, CO ₂ , O ₂ , N ₂		FYRITE/Orsat
Potential health and ecological effects	SASS ^e	Bioassay

^aFederal Register, 42(160):41776-41786, August 18, 1977.

^bAtomic absorption (AA) and inductively coupled argon plasma (ICAP) optical emission spectroscopy.

^cGas chromatography (GC)/mass spectrometry (MS).

^dGas chromatography (GC)/flame ionization detection (FID).

^eSource Assessment Sampling System.

TABLE 2. NUMBER OF GEOKINETICS GAS STREAM SAMPLES COLLECTED

Test	Demister inlet	Demister outlet	Incinerator exhaust gas
Method 5	1	1	1
Method 6	2	2	2
Method 7	2	2	2
Impinger trains:			
Ammonia (NH ₃)	1	1	1
Hydrogen cyanide (HCN)	1	1	1
Arsine (AsH ₃)	1	1	1
Grab (bag) samples:			
GC/FID	3	3	3
GC/MS	1	1	1
FYRITE/Orsat	3	3	3
Packed porous polymer tubes	3	3	3
SASS	- ^a	3	- ^a

^aNot selected for testing.

after being transported to the site, and the latter because of either breakthrough due to the presence of condensed hydrocarbon particles or the extreme temperature (about 650°C) of the incinerator exhaust.

Fugitive gas seepage through the retort overburden from small cracks and from around well casings was sampled using a specially designed collection system. The bag samples collected were analyzed for total hydrocarbons and C₁ through C₆ hydrocarbon fractions, leave as is carbon dioxide, carbon monoxide, and oxygen.

Bioassay Testing

The demister outlet gas and retort water were selected for biological testing in order to assess the health and ecological effects of untreated streams from *in-situ* oil shale retorting. The data that were obtained may be used as an aid in the selection and development of appropriate treatment facilities for retorting effluents. The number and type of bioassays on each sampling point are presented in Table 3; MRC, Litton Bionetics, and Los Alamos Scientific Laboratory performed the testing. The purposes of the specific bioassay tests are described briefly in Table 4, and the Level I biological analysis scheme used is depicted in Figure 7.

Water Sampling And Analysis

The retort water and evaporation pond water samples were composite samples based on EPA protocol [6], with modifications designed to better insure sample integrity and chain of custody and to fulfill site-specific requirements. These samples were analyzed for organic priority pollutants (except pesticides), trace elements, "conventional pollutants," and "water quality parameters." The "conventional pollutants" screened were chloride, bicarbonate, carbonate, cyanide, fluoride, nitrogen (ammonia, ammonium, Kjeldahl, nitrate, nitrite, and organic), phenols, total phosphorus, ortho phosphate, and sulfur (sulfate, sulfide, sulfite, tetrathionate, thiosulfate, and thiocyanate). The "water quality parameters" screened were alkalinity, biological oxygen demand, chemical oxygen demand, conductivity, hardness, oil and grease, pH, solids, and total inorganic and organic carbon. The

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- [6] Draft Final Report: Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants. U.S. Environmental Protection Agency, Cincinnati, Ohio, March 1977. 145 pp.

TABLE 3. NUMBER OF BIOLOGICAL TESTS OF GEOKINETICS SAMPLES

Bioassay	Demister outlet gas			
	Filter extract	Resin extract	Probe wash, condensate, and impinger water	Retort water
Mutagenicity:				
Ames	2	2	1	1
Cytotoxicity:				
RAM ^a	1	2	1	1
CHO ^b	2	2	1	1

^aRabbit alveolar macrophage cells.

^bChinese hamster ovary cells.

TABLE 4. PURPOSES OF BIOASSAY TESTS

Bioassay test	Purpose of test
Mutagenicity	Determination of whether a chemical mutagen (possibly a carcinogen) is present.
Cytotoxicity	Measure of metabolic impairment and death in mammalian cells.

APHA Standard Methods [7] were used to determine conventional pollutants and water quality parameters. It is recognized that there are interferences due to the complex matrix of pollutants in the water samples. However, no investigation of their effect on the analytical results was made, because methods development was considered to be beyond the scope of this project.

SAMPLING PROCEDURES

Gas Stream Sampling

Particulate Loading and Trace Elements --
A modification of the EPA Method 5 particulate sampling system was employed for particulate and trace elements. The basic Method 5 procedures and equipment used were those specified in

[7] Standard Methods for the Examination of Water and Wastewater, 14th edition. M. J. Taras, A. E. Greenburg, R. D. Dook, and M. C. Rand, eds. American Public Health Association, New York, New York, 1971. 874 pp.

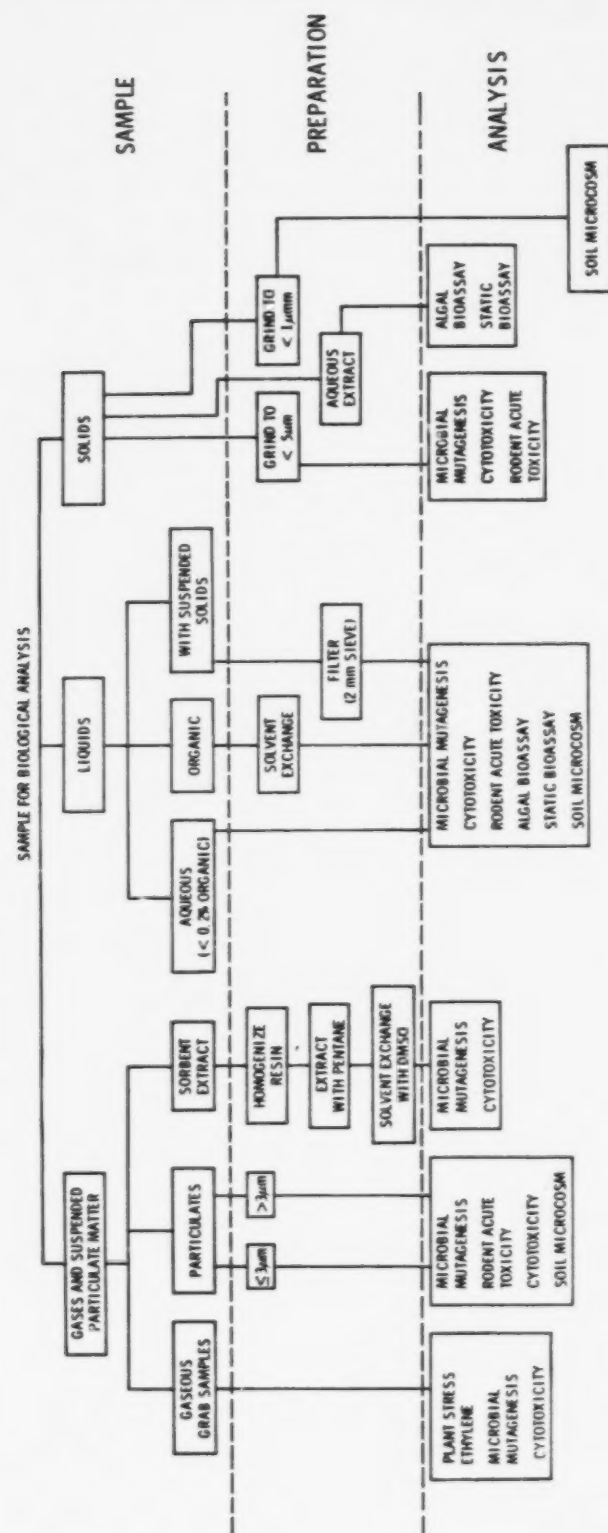


Figure 7. Level I biological analysis overview.

the Federal Register, 8 June 1976; however, the sampling train was modified to collect vapor phase inorganic materials along with the particulate [8].

The sampling system consisted of the Method 5 probe tip and probe assembly with a stainless steel liner. The probe was connected to a heated filter. The exit side of the filter was connected to the impingers. The impinger portion of the train was designed to collect vaporous inorganic species. Table 5 presents the impinger content and order.

TABLE 5. IMPINGER PORTION OF THE MODIFIED METHOD 5 TRAIN [9]

Impinger	Reagent ^a	Quantity	Purpose
1	30% H ₂ O ₂	100 mL	Trap reducing gases such as SO ₂ to prevent depletion of oxidative capability of other impingers.
2, 3	0.2M (NH ₄) ₂ S ₂ O ₈ + 0.02M AgNO ₃	200 mL (each)	Collect volatile trace elements by oxidative dissolution.
4	Silica gel	200 g	Prevent moisture from reaching pump and dry gas test meter.

^aM - molar; 1M = one mole of solute per liter of solution.

After selecting the minimum number of sampling points, the stack pressure, temperature, moisture, and range of velocity head were determined. Leak checking of the sampling train was accomplished by plugging the inlet to the filter holder and pulling 50.8 kPa (15 in. Hg) vacuum. A leakage rate less than 9.4×10^{-6} m³/s (0.02 ft³/min) at a vacuum of 50.8 kPa (15 in. Hg) was considered acceptable. Since the number of traverse points varied with the stack configuration, the duration of sampling at each point was determined by dividing the number of traverse points into the

- [8] Method 5 - Determination of Particulate Emissions from Stationary Sources. Federal Register, 41(111):23076-23083, 1976.
- [9] Lentzen, D. E., D. E. Wagoner, E. D. Estes, and W. F. Gutknecht. IERL-RTP Procedures Manual: Level 1 Environmental Assessment, Second Edition. EPA-600/7-78-201, U.S. Environmental Protection Agency, Washington, DC, October 1978. p. 74.

total run time (approximately two hours). Adjustments in the sampling flow rate were made at approximately 2-minute intervals in order to maintain isokinetic sampling conditions.

To begin sampling, the nozzle was positioned at the first traverse point with the tip pointing directly into the gas stream. Immediately, the pump was started and the flow adjusted to isokinetic conditions. Sampling was conducted for at least five minutes at each traverse point; sampling time was the same for each traverse point. Isokinetic sampling conditions were maintained throughout the sampling period using a nomograph when suitable, or using a computer program when conditions exceeded the capability of the nomograph. The pump was turned off at the conclusion of each run, and the final readings were recorded. After each run, the probe and nozzle were removed from the stack. These items, as well as the filter and impingers, were handled in accordance with approved sample recovery procedures.

The contents of each impinger were measured for liquid content and then transferred to bottles. Each impinger and the appropriate connecting lines, were rinsed with three portions of isopropyl alcohol and distilled water, and the rinses were added to the appropriate bottles. Figure 8 illustrates the modified Method 5 sampling train components and sample recovery procedures.

Organic Material Collection --

Grab samples of organic material were collected on porous polymer packed tubes and in Tedlar® bags. The porous polymer packed tube set-up consisted of a tube packed with XAD-2 resin, a tube packed with Tenax, and a glass flask. Samples were collected for periods of one to five minutes. The flasks were checked for organic content, and therefore "breakthrough," using a gas chromatograph with flame ionization detection. Also, grab (bag) samples were taken for organic compound analysis at the field site and at the Dayton Laboratory.

Hydrogen Cyanide, Ammonia, and Arsine --

Hydrogen cyanide (HCN), ammonia (NH₃), and arsine (AsH₃) were sampled by trapping in separate trains in solutions contained in fritted midget impingers (bubblers). The sampling trains consisted of a filter, four or five midget impingers, a rotometer, a dry gas test meter, and a pump. Flow rate and pressure were monitored at the rotometer to insure a known steady gas flow.

Table 6 summarizes the type of filter, number of impingers, impinger contents, gas flow rate, and sampling time for each compound.

Carbon Dioxide, Carbon Monoxide, Hydrocarbons, and Oxygen --

Integrated gas samples for the above components were collected as described in EPA Method 3, Gas Analysis for Carbon Dioxide,

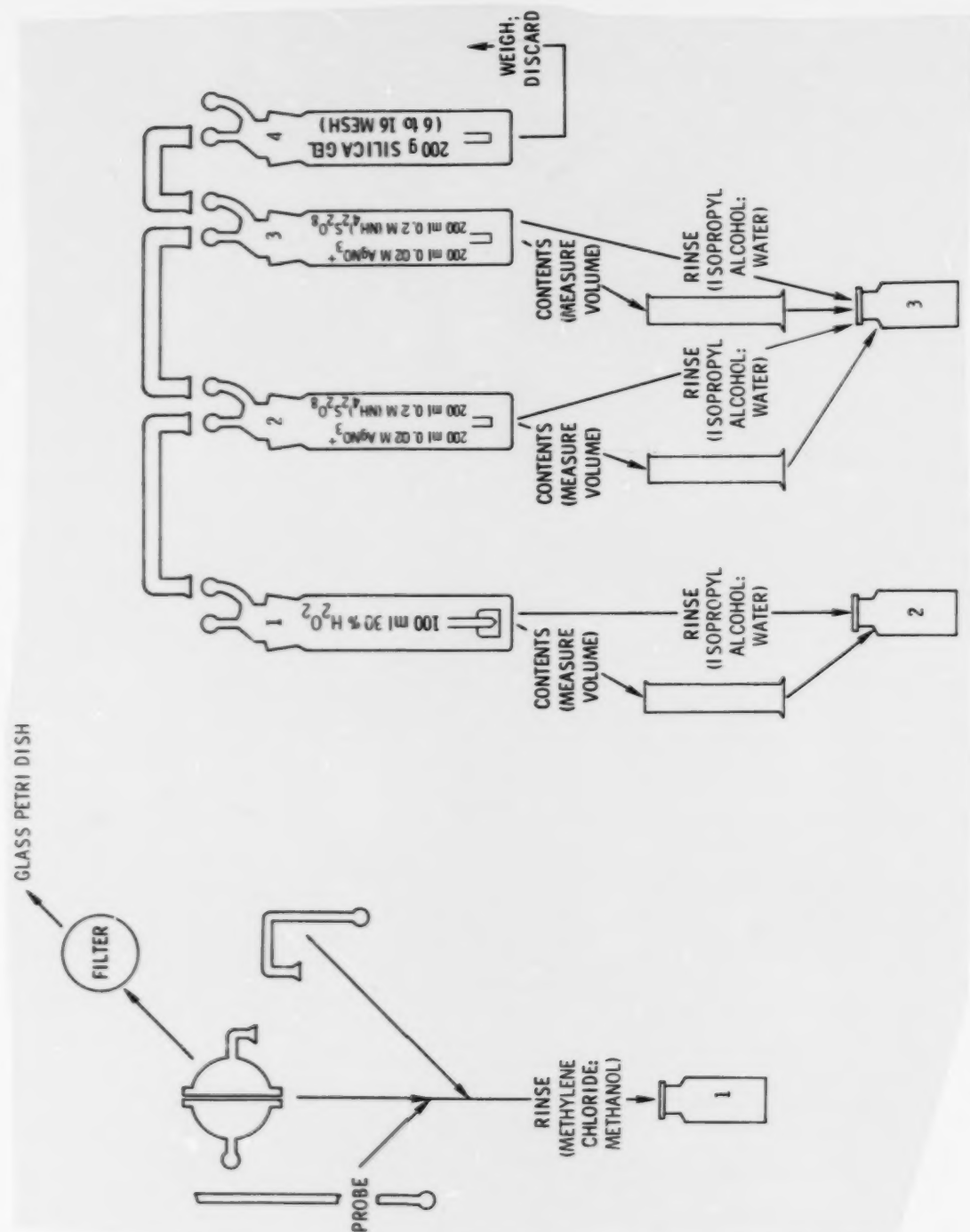


Figure 8. Modified Method 5 sampling train components and sample recovery procedures.

TABLE 6. COMPONENTS OF IMPINGER TRAINS FOR HYDROGEN CYANIDE, AMMONIA, AND ARSINE SAMPLING

Compound to be trapped	Sampling train components		Gas flow rate, cm ³ /min	Sampling period, min
	Filter	Number of impingers and contents		
Hydrogen cyanide [10]	Cellulose acetate	2 - 0.1M KOH	940	30
		1 - Glass wool		
		1 - Silica gel		
Ammonia [11]	Cellulose acetate	2 - 0.1N H ₂ SO ₄	940	30
		1 - Glass wool		
		1 - Silica gel		
Arsine	Cellulose acetate	1 - Cotton wool impregnated with lead acetate	940	30
		2 - 5% sodium hypochlorite		
		1 - Glass wool		
		1 - Silica gel		

Excess Air, and Dry Molecular Weight [12]. These samples were collected at approximately the same time as the Method 5 samples. The bags were leak-checked prior to sampling. To leak-check, a water manometer was connected to the bag, which was then pressurized to 50 to 100 mm H₂O. Any displacement of the water manometer within a 10-minute period indicated a leak. The material collected in the bags was used for on-site analysis of oxygen, carbon dioxide, carbon monoxide, total hydrocarbons, and specific C₁ to C₆ hydrocarbons.

- [10] Methods of Air Sampling and Analysis. Katz, M., ed. American Public Health Association, Washington, DC, 1972.
- [11] NIOSH Manual of Analytical Methods. U.S. Department of Health Education, and Welfare, Cincinnati, Ohio, 1974.
- [12] Method 3 - Gas Analysis for Carbon Dioxide, Excess Air, and Dry Molecular Weight. Federal Register, 41(111):23069-23070, June 1976.

Oxides of Nitrogen and Sulfur --

Nitrogen oxides (NO_x) were measured using EPA Method 7 [13]. Grab samples were taken at the beginning and end of each modified Method 5 run. Sulfur oxides (SO_x) were measured using EPA Method 6 [14].

Bioassay Samples --

The technique used to collect gas stream samples for bioassay testing was based upon that recommended by the EPA [7, 11], with site-specific modifications. The EPA protocol requires use of the Source Assessment Sampling System (SASS). The modifications to the SASS train were to remove the cyclones, which "size-fractionate" the particulate, and to remove the impinger systems, which collect vaporous organic material. The cyclones were removed and all particulate captured on the filter because information from Geokinetics personnel indicated that the particulate should be of small size. The impingers were not used because there are no recommended Level I bioassay tests for their contents due to the presence of oxidative reagents.

The modified SASS train (shown in Figure 9) consisted of a stainless steel probe, a heated oven module containing the filter, a solid sorbent (XAD-2 resin) trap, and a system for flow measurement and pumping. An impinger containing 750 grams of 3-8 mesh, color-indicating silica gel was placed before the pump to prevent moisture from reaching the pump.

Before sampling, the SASS train components were passivated with a 1:1 volumetric mixture of water and nitric acid. All surfaces associated with organic collection were cleaned with distilled water, isopropyl alcohol, and methylene chloride in succession. These components were then dried with a stream of purified air.

At the site, the train was assembled, and the oven was heated to 205°C (400°F) before each run. The resin trap was maintained at 20°C (68°F) during each run. A leak check was made before the start of each run; a leak rate of less than $23.6 \times 10^{-6} \text{ m}^3/\text{s}$ at 67.7 kPa (0.05 cfm at 20 in. Hg) was considered acceptable.

Fugitive Gas Sampling

Selection of Test Locations --

Geokinetics' explosive fragmentation of an oil shale deposit causes noticeable uplift of the surface of the overburden,

[13] Standards of Performance for New Stationary Sources. Federal Register, 36(247):24876-24895, 1971.

[14] Hamersma, J. W., S. L. Reynolds, and R. F. Maddalone. IERL-RTP Procedure Manual: Level I Environmental Assessment. EPA-600/2-76-160a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1976. 147 pp.

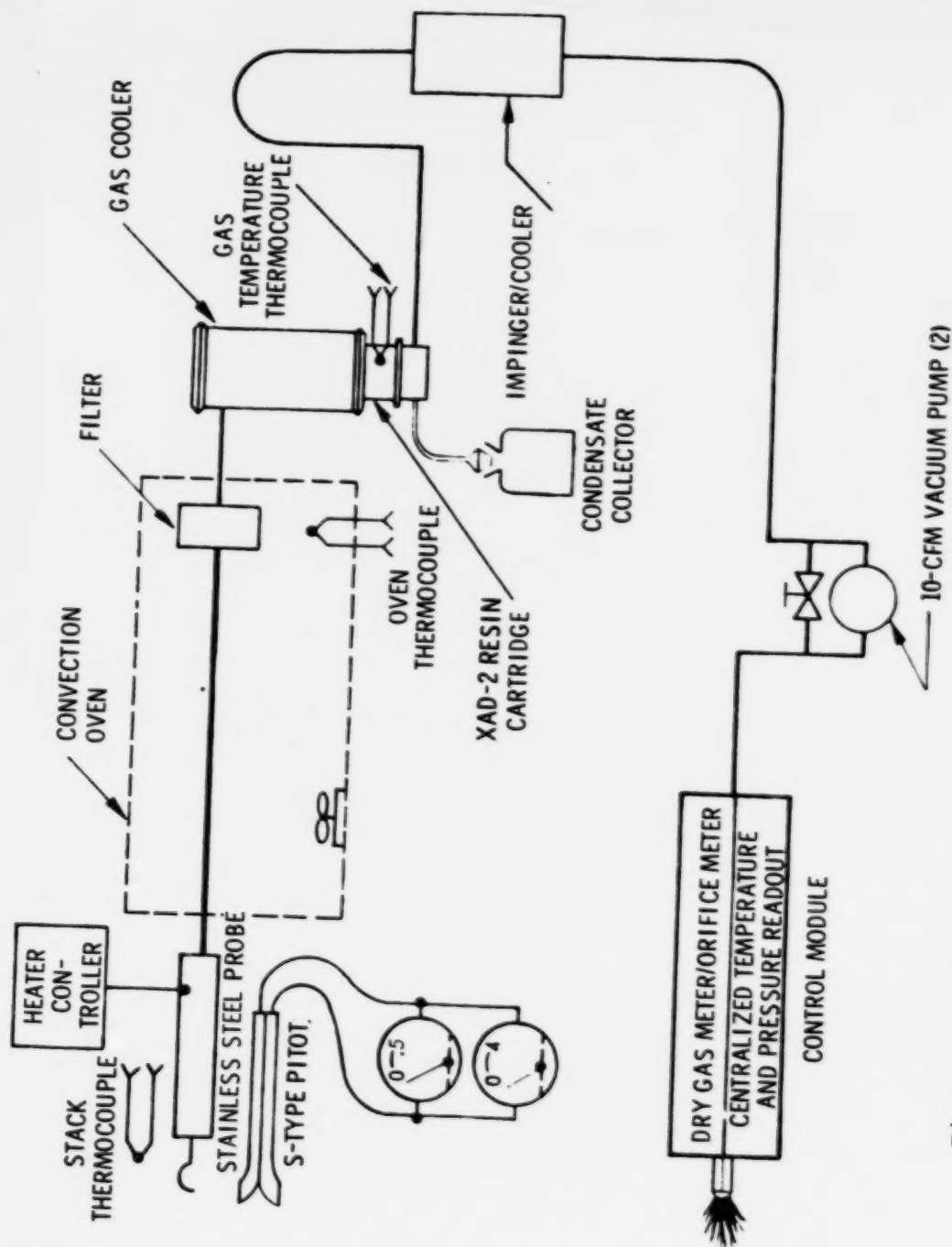


Figure 9. Schematic diagram of Source Assessment Sampling System.

creating ground cracks of various sizes. Plant personnel seal the larger cracks by wetting and tamping before retorting begins, but this does not eliminate all means of escape of gases from the burning retort. Additional sources of fugitive gas seepage are created by drilling and casing instrumentation wells into the oil shale bed. It has been estimated that as much as one-third to one-half of the total volume of gas injected is not recovered at the outlet wells (personal communication, S. G. Mankowski, Geokinetics, Inc., to W. R. Fearheller, Monsanto Research Corporation, February 13, 1979). The internal retort pressure is normally maintained between zero and two inches of water column. During MRC's testing, the pressure was maintained at a higher level to determine the maximum level of fugitive emissions.

In order to obtain representative data, test locations for fugitive gas sampling were randomly selected, with the constraint that an approximately equal number of sites be placed in each of four quadrants of the surface area of Retort No. 17. Locations for sampling ground seepage were selected by using a random number table corresponding to consecutively numbered squares on a grid superimposed over a scale diagram of the retort. Figure 10 shows the twenty-seven ground seepage sources (labeled G-1 through G-27), the six thermocouple wells (labeled T-1 through T-6), and one (P-1) of two shale oil production wells which were tested for fugitive emissions.

Dilution Sampling Methodology --

The fugitive emission sampling method used in this program represents a combination of the techniques developed by Monsanto Research Corporation and Washington State University under EPA Contract Nos. 68-02-1874 [15, 16] and 68-02-2071 [17], respectively. The selected sources were first prepared for sampling by "tenting." The tent enclosure consisted of an aluminum box, 0.61 m (2 ft) square, with an open top and bottom, a sheet of plastic, and duct tape. The aluminum box was driven into the soil

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- [15] Hughes, T. W., D. R. Tierney, and Z. S. Khan. Measuring Fugitive Emissions from Petrochemical Plants. Chemical Engineering Progress, 75(8):35-39, 1979.
 - [16] Tierney, D. R., L. B. Mote, Z. S. Khan, and T. W. Hughes. Source Assessment: Fugitive Hydrocarbon Emissions from Petrochemical Plants - Summary Report (draft report). U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1979. 79 pp.
 - [17] Zimmerman, P. Procedures for Conducting Hydrocarbon Emission Inventories of Biogenic Sources and Some Results of Recent Investigations (paper presented at the 1977 EPA Emission Inventory/Factor Workshop, Raleigh, North Carolina, September 1977). 28 pp.

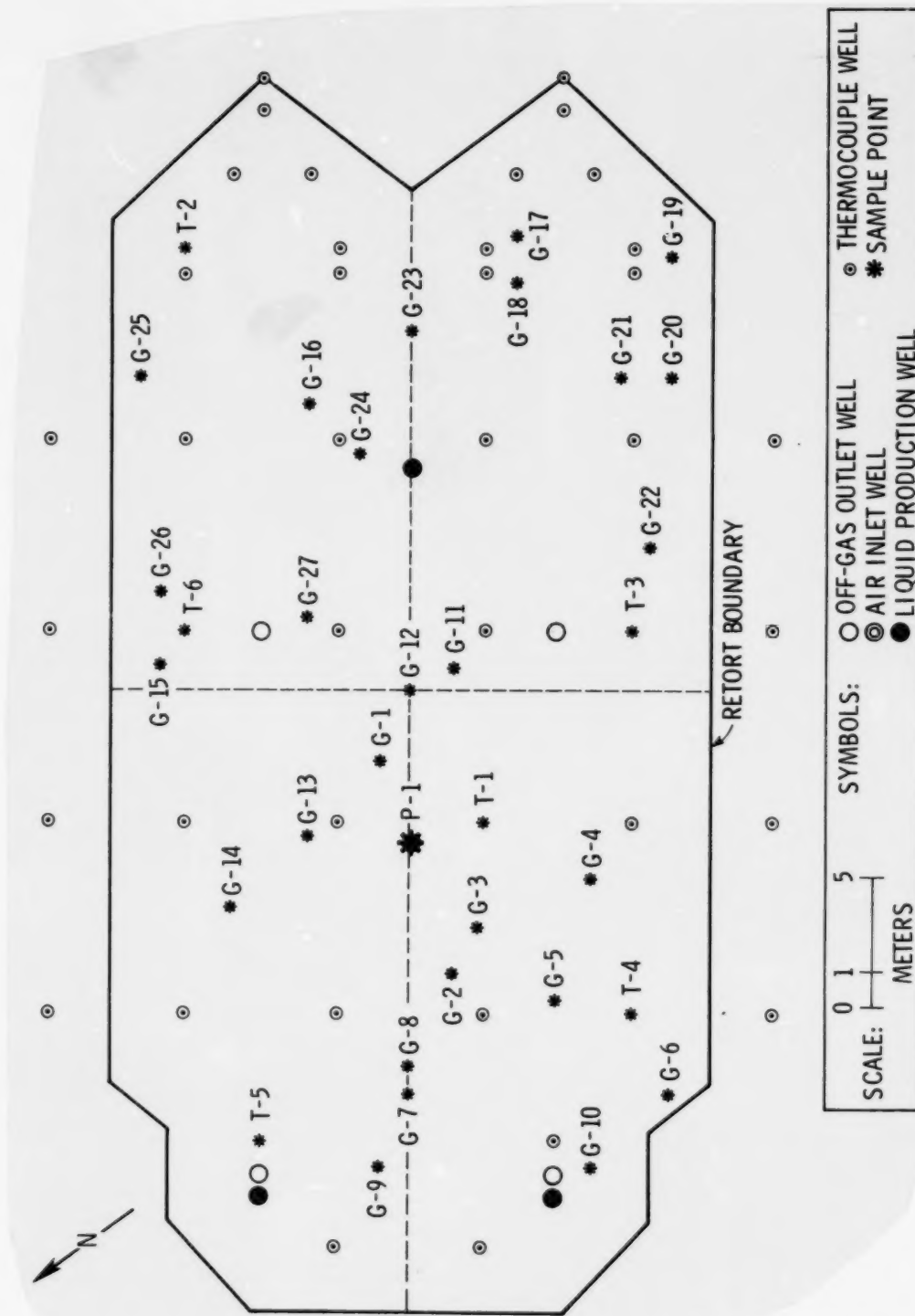


Figure 10. Location of fugitive emission sampling points on Retort No. 17.

and anchored at all four corners with metal rods; moist soil was used outside the bottom of the sampling box to provide a satisfactory seal to the surface. The top of the box was covered with flexible plastic, attached to the sides by duct tape.

The fugitive emission sampling train, mounted on a portable cart for maneuverability, was then connected to the tented source with Teflon® tubing. The sampling train was equipped with a calibrated orifice meter and a manometer to measure the flow rate of dilution air and a thermometer to provide readings of ambient air temperature. The sample box outlet was connected, via a three-way valve, to a 500-mL glass syringe and to a vacuum pump. This pump was used to evacuate the aluminum and plastic tent for approximately five minutes prior to sample collection. The complete system, ready to begin sampling of fugitive emissions from Geokinetics Retort No. 17, is shown in Figure 11. The tent enclosure is flanked, on the right, by the glass syringe (and, in the right foreground, a temperature/pressure well pair) and, on the left, by the sampling cart and a cylinder of purified compressed air.

Figure 11. Fugitive emission sampling apparatus for measurement of gas seepage at Geokinetics Retort No. 17.

The sampling tent was then filled with air, free of hydrocarbons and carbon dioxide, supplied by a pressurized cylinder at 10 liters per minute, as determined by the manometer pressure drop. As soon as this input of dilution air was begun, the three-way valve was turned so as to allow inflation, and the vacuum pump was shut off and replaced with a Teflon® sample bag, 0.3 m (1 ft) square. The sampling tent was partially inflated for five minutes, at which time a sample was obtained by using the syringe to inject gas into the Teflon® bag. After its contents were analyzed using a track-mounted gas chromatograph, the sample bag was prepared for reuse by filling with gas chromatograph-grade nitrogen followed by drawing a vacuum, this sequence being repeated three times.

Water Sampling

A grab sampling technique was used to composite samples for priority pollutant analysis from the two sampling locations previously described. The technique is based upon that recommended by the EPA in Reference 6, with modifications designed to better insure sample integrity, maintain chain of custody, and fulfill site-specific requirements. The EPA sampling protocol requires compositing samples into a 9.5 L to 11.4 L (2.5 gal to 3 gal) glass bottle using an automatic sampler. This composite sample is then distributed to the appropriate sample bottles and used for analysis of the following groups of priority pollutants: base/neutral organics, acid organics, pesticides, polychlorinated biphenyls (PCBs), and metals. A single grab sample is recommended in the EPA protocol for each of the following priority pollutant groups: volatile organics, cyanides, and phenols. MRC's grab sampling technique differs from EPA's in that it allows for compositing directly into the appropriate sample containers for priority pollutant analyses, as follows: 1) 3.8 L (1 gal) glass bottle for base/neutral organics, acid organics, pesticides, and PCB's; 2) 500 mL plastic bottle for metals; 3) 1 L glass bottle for phenols; and 4) 500 mL plastic bottle for cyanide. By initially adding the proper preservatives to each bottle and maintaining the samples at a temperature of about 4°C, this technique allowed for collecting composited samples for phenols and cyanide as opposed to collecting a single grab sample for each. MRC's grab sampling technique also allows for metals samples to be collected in plastic containers instead of glass bottles, thus reducing the loss of metals due to adsorption onto glass walls and leaching of metals from the glass.

Samples were collected using a 11.4 L (3-gal) Teflon-lined stainless steel bucket. A specified aliquot was transferred to each of the sample bottles from the container. Care was taken to prevent contamination and to insure that the sample remained homogeneous. Separate glassware was used at the sample location to avoid cross-contamination of samples. During the first grab sampling period, each sample container was "seasoned" by rinsing

with the appropriate wastewater sample and discarding the rinse. All samples were stored on ice for the entire sampling period.

MRC's collection technique for volatile organics again differs slightly from the EPA protocol, which calls for one grab sample (plus one duplicate) during the sampling period. Due to the nature of the volatile sample, a grab sample must be taken and immediately sealed hermetically. Because the one-sample concept is in conflict with compositing over a 24-, 48-, or 72-hour period, MRC's technique consisted of collecting several volatile samples and compositing them at the Dayton Laboratory for one analysis.

Table 7 shows the priority pollutant sample volumes collected, the containers used to hold the samples, and the needed preservations. Composite samples for "conventional pollutants" and "water quality parameters" to be analyzed were collected at the same time as the priority pollutant samples in appropriately cleaned sample containers, as given in Standard Methods [7].

Upon completion of the sampling period, the pH of each preserved sample was checked to insure proper sample preservation. Each bottle cap was sealed with tape to prevent leakage during shipment. All glass bottles were individually wrapped with glass-packing material and placed in metal or molded plastic chests, which were filled with ice to maintain the sample temperature at 4°C. The ice chests were taped shut, appropriate shipping labels were applied, and the samples transported by truck to MRC's Dayton Laboratory for subsequent analysis. MRC judged this sample handling procedure to be adequate for the purposes of the screening program.

ANALYTICAL PROCEDURES

Gas Stream Samples

Particulate Mass Loading --

The amount of particulate collected in the modified EPA Method 5 train was determined from the material collected by the filter and that which was rinsed from the probe tip, probe, and connecting glassware. In order to determine the mass loading, the filter was desiccated to dryness and weighed. The original filter weight was then subtracted from the final weight in order to calculate the mass of particulate collected. The probe and connecting glassware washes were evaporated to dryness using a technique designed to minimize loss of organic material from the particulates, and the residue was weighed. The residue weight plus the filter catch provided the mass for calculating the particulate loading in the gas stream sampled.

TABLE 7. PRIORITY POLLUTANT SAMPLING LOGISTICS

Type of test	Type of bottle	Sample size	Number of bottles per point	Preservatives required (7, 14)
Volatile organics	 glass vial with Teflon-lined septum	40 ml	2	Keep at 4°C. If residual chlorine is present (determined using potassium-iodide paper) add 0.03 ml of 10% sodium thiosulfate to each vial.
Nonvolatile organics (base/ neutrals, pesticides, and PCB's)	 amber glass pharmaceutical jug with Teflon-lined cap	1 gallon	1	Keep at 4°C.
Metals	 plastic bottle	500 ml	1	Keep at 4°C. In the lab add redistilled HNO ₃ to pH <2.
Cyanide (total)	 plastic bottle	500 ml	1	Keep at 4°C. Adjust pH ≥12 with 10N NaOH.
Phenol (total)	 amber glass bottle	1 liter	1	Keep at 4°C. Adjust pH ≤4 with concentrated H ₂ SO ₄ .

Elemental Analysis --

Analyses of elemental composition were performed on samples taken with the modified Method 5 train and on water samples. The particulates recovered from the probe were expected to be of the same composition as those on the filter and therefore were not analyzed. Atomic absorption was used to analyze arsenic, mercury, selenium, and thallium. The AtomComp technique, employing an inductively coupled argon plasma (ICAP) excitation source, was used to quantify aluminum, antimony, barium, beryllium, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, phosphorus, potassium, silicon, silver, sodium, strontium, tin, titanium, vanadium, and zinc.

Mercury and thallium were determined by flameless atomic absorption. Arsenic and selenium were determined by conversion to their hydrides and aspiration into an argon-hydrogen flame. A detailed description of these methods can be found in Reference 18.

The Jarrell-Ash AtomComp with ICAP excitation forms an analytical system for simultaneous multielement determinations of trace metals at the sub-ppm level in solutions. The basis of the method is atomic emission promoted by coupling the sample, nebulized to form an aerosol, with high-temperature argon gas produced by passage of argon through a powerful radio-frequency field [19].

Aqueous impinger solutions from the modified EPA Method 5 sampling train were analyzed for the volatile elements, that is, antimony, arsenic, cadmium, lead, mercury, and selenium, which might not be completely collected by the filter. All of the filter samples were digested before analysis, using the technique originally developed by Bernas and modified by Hartstein for trace metal analyses of coal dust using atomic absorption [20, 21]. This

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- [18] Metals by Atomic Absorption Spectrophotometry. In: Standard Methods for the Examination of Water and Wastewater, 14th Edition. American Public Health Association, Washington, DC, 1976. 1,193 pp.
 - [19] Jarrell-Ash Plasma AtomComp for the Simultaneous Determination of Trace Metals in Solutions (manufacturer's brochure). Catalog 90-975, Jarrell-Ash Company, Waltham, Massachusetts. 5 pp.
 - [20] Bernas, B. A New Method for Decomposition and Comprehensive Analysis of Silicates by Atomic Absorption Spectrometry. Analytical Chemistry, 40(11):1682-1686, 1968.
 - [21] Hartstein, A. M., R. W. Freedman, and D. W. Platter. Novel Wet-Digestion Procedure for Trace-Metal Analysis of Coal by Atomic Absorption. Analytical Chemistry, 45(3):611-614, 1973.

method employs the Parr 4145 Teflon-lined bomb and involves digestion of powdered samples in ULTRAR brand (69% to 71%) redistilled nitric acid at 150°C. The accuracy of this method for coal dust analysis, reported for 10 metals, ranged from 94% for beryllium to 106% for nickel using 10-mg samples. Sample solutions produced by acid digestion were diluted to 250 milliliters with distilled water, to reduce acid concentrations to approximately 2%, and submitted for analysis.

Organic Analysis --

The porous polymer packed tube samples, along with a blank, were analyzed for organic materials by gas chromatography (GC) and mass spectrometry (MS). Solvent desorption with pure methanol was used on both the XAD-2 tubes and the Tenax tubes for sample recovery. The analyses were performed on a Hewlett-Packard 5982A GC/MS system, which is comprised of the following:

- HP 5982A Mass Spectrometer--dodecapole with vacuum system and control unit, GC/MS membrane interface, and heated expansion volume inlet.
- Chemical ionization source and gas manifold system.
- Direct induction probe.
- HP 5780A Gas Chromatograph with digital oven programmer for subambient operation with nitrogen (N₂) and heated gas sampling valve.
- HP 5933A Data System--8K computer with dual disk memory (capacity for 0.5 million spectra per disk), Aldermaston Spectra Library (12,800 spectra), complete software package of HP Mass, and standard computer programs.
- High-speed plotter, cathode ray tube (CRT) graphic display, and hard copier.

Selected bag samples were returned to the Dayton Laboratory for analysis using the Hewlett-Packard 5982A GC/MS system. Other bag samples were analyzed on site for total hydrocarbons and C₁ to C₆ hydrocarbon fractions. The analyses were performed using an AID portable chromatograph with a flame ionization detector (FID), and a 1.8 m x 3.2 mm (6 ft x 1/8 in.) stainless steel column packed with Porapak Q, 80 to 100 mesh. Total hydrocarbon content was determined by bypassing the GC and injecting directly into the detector.

Hydrogen Cyanide, Ammonia, and Arsine --

Impinger solutions were analyzed for hydrogen cyanide (HCN) using APHA Standard Methods [7]. An Orion ion-selective electrode method for ammonium ion (NH₄⁺) was used to analyze the ammonia

impinger solutions. Arsine concentrations in the impinger solutions were determined using atomic absorption.

Carbon Dioxide, Carbon Monoxide, Oxygen, and Water --

During the modified Method 5 particulate and trace metal sampling, gaseous samples were collected using EPA Method 3, "Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight" [12]. The samples collected in Tedlar® bags were analyzed on site by the Orsat technique for carbon monoxide, carbon dioxide, and oxygen. The moisture content of the gas stream was obtained from the Method 5 particulate-trace metal sampling train impinger contents. The increase in liquid level in the impinger was measured, prior to rinsing the impinger with solvent and placing the liquid and rinses into a bottle.

Oxides of Nitrogen and Sulfur --

Samples collected by Method 7 for NO_x analysis were partially worked up at the test site by recording flask temperature, barometric pressure, and internal flask pressure after the flask and contents had set for at least 16 hours and had been shaken for two minutes. Flask contents were transferred to polyethylene containers, sealed, and returned to the Dayton Laboratory for analysis using the Federal Register procedure [13].

Method 6 samples for SO_x analysis were sealed in polyethylene containers and refrigerated in the field for shipment to MRC's Dayton Laboratory. At the laboratory, the samples were analyzed as specified in the Federal Register, without considering the possible interference by ammonia [13].

Bioassay Testing --

Biological testing for a preliminary assessment of health and ecological effects of oil shale retorting emissions and effluents was conducted by three organizations - Los Alamos Scientific Laboratory (LASL), Litton Bionetics, and MRC. All tests were performed as specified in the IERL-RTP Procedures Manual: Level I, Environmental Assessment Biological Tests for Pilot Studies [22], or equivalent. Table 8 summarizes the preliminary biological test matrix for each organization. LASL analyzed both demister outlet gas and retort water samples. Litton and MRC analyzed demister outlet gas samples only.

[22] Duke, K. M., M. E. Davis, and A. J. Dennis. IERL-RTP Procedures Manual: Level I, Environmental Assessment Biological Tests for Pilot Studies. EPA-600/7-77-043, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1977. 119 pp.

TABLE 8. PRELIMINARY BIOASSAY TEST MATRIX

Bioassay	LASL	Litton	MRC
Media ^a	2	1	1
Mutagenicity: Ames	✓	✓	✓
Cytotoxicity: RAM CHO		✓ ✓	✓

^aMedia: 1 - Demister outlet gas samples.
2 - Retort water samples.

Fugitive Gas Samples

The content of the grab sample bags used in the fugitive emission sampling train were analyzed on site for both total hydrocarbons and C₁ to C₆ fractions using the methods described previously. Selected bag samples were also analyzed for CO₂, CO, and O₂ using the previously discussed techniques.

Water Samples

Conventional Pollutants and Water Quality Parameters --
The water sample characteristics listed previously in this section were measured using APHA Standard Methods [7]. Spikes, blind repeats, and blanks were utilized in the analyses. The validity of the standard methods is in doubt when applied to oil shale retorting water samples; however, those methods were used instead of developing new techniques owing to the screening nature of this program.

Priority Pollutants --
Recommended procedures [6] developed by the EPA were used for priority pollutant analyses. The EPA protocol [14] divides the 129 priority pollutants into three basic categories: volatile organics, nonvolatile organics, and metals. The following sections outline the analytical procedures and MRC modifications for volatile and nonvolatile organics. Analytical procedures for metals were discussed previously. Pesticides were not determined in this project.

Volatile Organics--The recommended analytical method was designed to determine those chemical species which are amenable to the Bellar purge and trap method. Volatile organics from 5 x 10⁻⁶ m³ samples of composite solution were sparged with helium onto two Tenax GC-silica-packed sample tubes, along with internal standards

added to the solutions. The second Tenax tube was used as a back-up sample. Tenax tubes were sealed under a nitrogen atmosphere in glass tubes and stored in a freezer at -18°C until analyzed.

Analyses were carried out using a Hewlett-Packard 5981 GC-Mass Spectrometer with a 5934 Data System. Sample tubes were heated to 180°C over a 1-minute period and held at that temperature for 4 minutes to desorb the compounds onto a Carbowax 1500 column held at -40°C . After desorption, the GC column temperature was raised $8^{\circ}\text{C}/\text{min}$ to 170°C .

The mass spectrometric analysis method involves fragmentation of molecules using electron bombardment (70eV). Masses and relative intensities of the most characteristic molecular fragments for each compound are listed in the protocol [6]. The population of ion fragments covering the mass range from 35 atomic mass units to 500 atomic mass units was measured every six seconds, and the data were stored on magnetic tape. These data allowed the operator to reconstruct chromatograms of observed intensity for an individual mass during the course of the scanning. Specific molecules may be detected in the presence of other compounds by examining the reconstructed intensity time plots of their characteristic masses.

Qualitative identification of a compound was made using the three criteria listed in the protocol: 1) retention time must coincide with known retention times; 2) the three characteristic masses must elute simultaneously; and 3) intensities of the characteristic masses must stand in the known proper proportions. Response ratios using the 1,4-dichlorobutane internal standard were used in quantifying the concentrations. Base/neutral and acid organic compounds were quantified using deuterated anthracene and response ratios as prescribed in the protocol [6].

Nonvolatile Organics--The method used for nonvolatile organics determined the nonvolatile solvent-extractable organic compounds that could be analyzed by gas chromatographic methods. The 129 priority pollutants include 81 organic compounds classified as nonvolatile organics. Nonvolatile organics are divided into three groups: base/neutral fraction, acid fraction (phenols), and pesticides and polychlorinated biphenyls (PCBs).

The analytical procedure for nonvolatile organics is described in Reference 6. Figure 12 depicts the sample processing scheme for the base/neutral and acid fractions. Each sample solution (0.002 m^3) was made alkaline (pH greater than 11) using sodium hydroxide, after which it was extracted three times using methylene chloride. Extracts were dried on a column of anhydrous sodium sulfate, concentrated to 10^{-6} m^3 in a Kuderna-Danish evaporator with a Snyder column, spiked with deuterated anthracene, sealed in septum-capped vials, and stored at 4°C until analyzed.

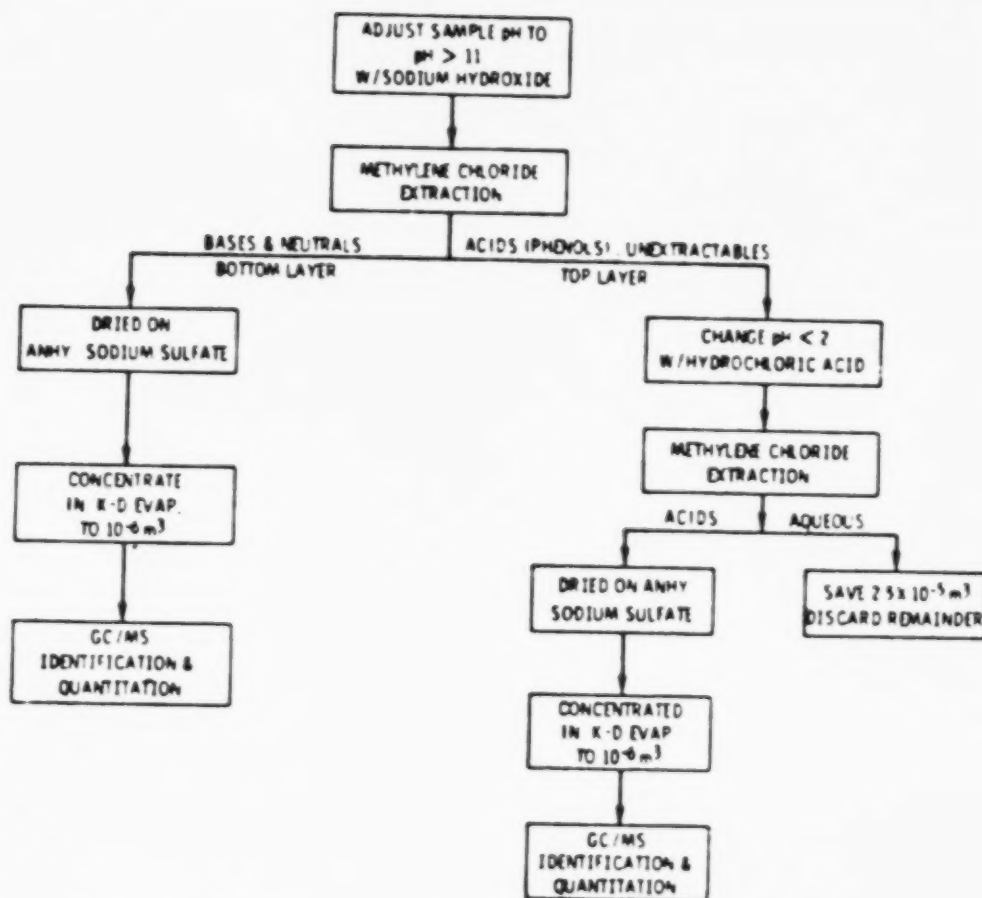


Figure 12. Analytical scheme for nonvolatile organic analysis. Analyses were performed on a GC/MS system using SP 2250 and Tenax GC columns for base/neutral and acid samples, respectively [7].

SECTION 5

RESULTS AND DISCUSSION

AIR POLLUTANT EMISSIONS

Process and Stack Gas Streams

Criteria Pollutants --

Particulate matter and carbon monoxide--Particulate matter, determined using a modification of EPA Method 5, was the first of five criteria pollutants measured in gas stream samples from Geokinetics' *in-situ* oil shale retorting facility. Tables 9 (metric units) and 10 (English units) provide complete computer-generated results of Method 5 tests of the demister inlet, the demister outlet and the incinerator exhaust. Stack characterization parameters from Table 9, obtained using EPA Methods 1 and 2, are summarized in Table 11.

EPA Method 3 analyzes for carbon dioxide, carbon monoxide, another criteria pollutant, and oxygen by the Orsat technique; the resulting molecular weight determination is another prerequisite for performing Method 5. Raw data from Orsat analysis of the three sample points at Geokinetics Retort No. 17 are listed in Table 12 and summarized in Table 13. Note that, although the discharge of carbon monoxide directly from the burning retort is considerable (on the order of 100 kg/hr), none of this criteria pollutant is emitted to the atmosphere because of complete combustion in the incinerator.

Quantitative results from Method 5 tests of gas streams from Geokinetics Retort No. 17 are given in Table 14. Geokinetics personnel contend that a substantial fraction of the reported particulate matter consists of condensed organic compounds as opposed to inorganic solids such as shale dust (personal communication, H. K. Spradlin, Geokinetics, Inc., to G. M. Rinaldi, Monsanto Research Corporation, October 30, 1979). Nevertheless, the incinerator exhaust gases contain a residual loading of 0.028 g/m³, corresponding to a particulate emission rate of 0.43 kg/hr, or a reduction of approximately 60 percent relative to the demister outlet gases. Extrapolating all the above conditions to Geokinetics' projected full-scale operations producing 320 m³ (2,000 bbl) of shale oil each day [2], particulate

TABLE 9. STACK CHARACTERIZATION AND PARTICULATE
SAMPLING DATA (METRIC UNITS)

ABBR	DESCRIPTION (20 DEG C)	UNITS	DEMISTER INLET	DEMISTER OUTLET	INCINERATOR EXHAUST
TT	DURATION OF RUN	MINUTES	62.0	124.0	124.0
PB	BAROMETRIC PRESSURE	CM HG	59.99	59.94	59.99
DELH	AVG ORIFICE PRESS DROP	CM H2O	1.877	2.566	3.117
VM	VOL DRY GAS(METER CON)	DCM	0.967	2.245	2.427
TM	AVG GAS METER TEMP	DEG C	42.2	35.1	34.6
VMSTD	VOL DRY GAS (STD COND)	DNCM	0.71	1.69	1.83
VW	TOTAL H2O COLLECTED	ML	87.9	271.3	154.1
VWG	VOL H2O VAPOR(STD CON)	NCM	0.117	0.362	0.206
PCNTM	PERCNT MOISTURE BY VOL		14.15	17.64	10.09
MD	MOLE FRACTION DRY GAS		0.859	0.824	0.899
CO2	PERCENT CO2		23.0	23.0	12.2
O2	PERCENT O2		0.2	2.2	4.6
N2	PERCENT N2		68.4	70.3	82.9
MWD	MOL WT OF DRY GAS		31.5	31.7	30.1
MW	MOL WT OF STACK GAS		29.6	29.3	28.8
DELP	AVG STACK VELOCITY HEAD	CM H2O	0.779	0.453	0.226
CP	PITOT COEFFICIENT		0.780	0.780	0.780
TS	STACK TEMPERATURE	DEG C	64.	51.	677.
PM	STACK PRESSURE(STATIC)	CM H2O	12.70	-0.10	-0.20
PS	STACK PRESSURE (ABS)	CM HG	60.93	59.94	59.98
VS	AVG STACK GAS VELOCITY	MPH	624.	472.	574.
DS	STACK DIAMETER	CM	25.40	25.40	74.68
AS	STACK AREA	SQ CM	506.7	506.7	4380.0
QS	STACK FLOW RT(DRY STD)	DNCMPM	19.	14.	55.
QA	STACK FLOW RT(ACTUAL)	ACMPM	32.	24.	251.
DN	PROBE TIP DIAMETER	CM	0.610	0.775	1.227
PCTI	PERCENT ISOKINETIC		105.2	104.2	99.5
MF	PARTICULATE (FRONT)	MG	1244.40	2163.20	237.30
MT	PARTICULATE (TOTAL)	MG	1244.40	2163.20	237.30
CAN	PARTICULATE (FRONT)	G/DNCM	1.7459	1.2782	0.1293
CAO	PARTICULATE (TOTAL)	G/DNCM	1.7459	1.2782	0.1293
CAT	PARTICULATE (FRONT)	G/ACM	1.0465	0.7509	0.0283
CAU	PARTICULATE (TOTAL)	G/ACM	1.0465	0.7509	0.0283
CAW	PARTICULATE (FRONT)	KG/HR	1.991	1.081	0.428
CAX	PARTICULATE (TOTAL)	KG/HR	1.991	1.081	0.428

TABLE 10. STACK CHARACTERIZATION AND PARTICULATE SAMPLING DATA (ENGLISH UNITS)

ABBR	DESCRIPTION (68 DEG F)	UNITS	DEMISTER INLET	DEMISTER OUTLET	INCINERATOR EXHAUST
TT	DURATION OF RUN	MINUTES	62.0		
PB	BAROMETRIC PRESSURE	IN HG	23.62	124.0	124.0
DELH	AVG ORIFICE PRESS DROP	IN H2O	0.739	23.60	23.62
VM	VOL DRY GAS(METER CON)	DCF	34.146	1.010	1.227
TM	AVG GAS METER TEMP	DEG F	107.9	79.270	85.685
VMSTD	VOL DRY GAS (STD COND)	DSCF	25.12	95.2	94.3
VW	TOTAL H2O COLLECTED	MI	87.9	59.65	64.69
VWG	VOL H2O VAPOR(STD CON)	SCF	4.140	271.3	154.1
PCNTM	PERCNT MOISTURE BY VOL		14.15	12.778	7.258
MD	MOLE FRACTION DRY GAS		0.859	17.64	10.09
CO2	PERCENT CO2		23.0	0.824	0.899
O2	PERCENT O2		0.2	23.0	12.2
N2	PERCENT N2		68.4	2.2	4.6
MWD	MOL WT OF DRY GAS		31.5	70.3	82.9
MW	MOL WT OF STACK GAS		29.6	31.7	30.1
DELP	AVG STACK VELOCITY HEAD	IN H2O	0.307	29.3	28.8
CP	PITOT COEFFICIENT		0.780	0.178	0.089
TS	STACK TEMPERATURE	DEG F	146.	0.780	0.780
PM	STACK PRESSURE(STATIC)	IN H2O	5.00	124.	1251.
PS	STACK PRESSURE (ABS)	IN HG	23.99	-0.04	-0.08
VS	AVG STACK GAS VELOCITY	FPM	2047.	23.60	23.61
DS	STACK DIAMETER	INCHES	10.00	1549.	1883.
AS	STACK AREA	SQ IN	78.5	10.00	29.40
QS	STACK FLOW RT(DRY STD)	DSCFM	672.	78.5	678.9
QA	STACK FLOW RT(ACTUAL)	ACFM	1116.	498.	1951.
DN	PROBE TIP DIAMETER	INCHES	0.240	845.	8874.
PCTI	PERCENT ISOKINETIC		105.2	0.305	0.483
MF	PARTICULATE (FRONT)	MG	1244.40	104.2	99.5
MT	PARTICULATE (TOTAL)	MG	1244.40	2163.20	237.30
CAN	PARTICULATE (FRONT)	GR/DSCF	0.7628	2163.20	237.30
CAO	PARTICULATE (TOTAL)	GR/DSCF	0.7628	0.5584	0.0565
CAT	PARTICULATE (FRONT)	GR/ACF	0.4572	0.5584	0.0565
CAU	PARTICULATE (TOTAL)	GR/ACF	0.4572	0.3281	0.0124
CAW	PARTICULATE (FRONT)	LB/HR	4.390	0.3281	0.0124
CAX	PARTICULATE (TOTAL)	LB/HR	4.390	2.384	0.944
				2.384	0.944

TABLE 11. REPRESENTATIVE VALUES OF STACK CHARACTERIZATION PARAMETERS^a

Parameter	Units	Sample point		
		Demister inlet	Demister outlet	Incinerator outlet
Diameter	cm	25.4	25.4	74.6
Cross-sectional area	cm ²	507	507	4,370
Temperature	°C	64	51	677
Static pressure	kPa	1.2	-0.01	-0.02
Absolute pressure	kPa	81.2	79.9	79.9
Average gas velocity	m/min	624	472	574
Average velocity head	Pa	76	44	22
Gas flow rate				
Dry, standard conditions	m ³ /hr	1,140	846	3,310
Actual conditions	m ³ /hr	1,900	1,440	15,070

^a Determined during EPA Method 1 and 2 sampling runs.

TABLE 12. ORSAT ANALYSIS OF GAS STREAMS FROM GEOKINETICS RETORT NO. 17^a

Sample point	Sample number	Concentration (dry basis), percent by volume		
		Carbon dioxide (CO ₂)	Oxygen (O ₂)	Carbon monoxide (CO)
Demister inlet	1	23.0	1.2	6.2
		23.0	1.2	6.2
	2	22.0	2.0	5.8
		22.0	2.0	5.8
	3	23.9	0.2	7.9
		23.4	0.2	7.5
Demister outlet	1	23.8	1.4	5.8
		23.8	1.4	5.8
	2	23.0	2.2	4.4
		23.0	2.3	4.4
		23.0	2.3	4.4
	3	19.8	3.0	5.2
		19.8	3.0	5.0
		19.8	3.0	5.2
		19.8	3.0	5.2
		19.8	3.0	5.2
Incinerator outlet	1	10.0	5.2	0
		10.0	5.2	0
		9.8	5.2	0
	2	9.6	6.2	0
		10.0	5.8	0
		9.8	6.0	0
	3	12.2	4.6	0
		12.2	5.0	0
		12.2	5.0	0
		12.2	5.0	0

^a Table entries are multiple analyses of multiple samples.

TABLE 13. AVERAGE CONCENTRATIONS OF CO₂, O₂, AND CO IN GAS STREAMS FROM GEOKINETICS RETORT NO. 17

Sample point	Concentration (dry basis), percent by volume			Mass flow rate of carbon monoxide, ^a kg/hr
	Carbon dioxide (CO ₂)	Oxygen (O ₂)	Carbon monoxide (CO)	
Demister inlet	22.9	1.1	6.6	100
Demister outlet	22.2	2.2	5.1	61
Incinerator outlet	10.6	5.4	0	0

^aCalculated using dry gas flow rates at actual conditions.

TABLE 14. QUANTIFICATION OF PARTICULATE MATTER IN GAS STREAMS FROM GEOKINETICS RETORT NO. 17

Sample point	Particulate mass collected ^a , g			Concentration in gas stream, ^b g/m ³	Mass flow rate, kg/hr
	Filter	Probe wash	Total		
Demister inlet	0.400	0.844	1.244	1.0	2.0
Demister outlet	0.453	1.710	2.163	0.75	1.1
Incinerator outlet	0.081	0.156	0.237	0.028	0.43

^aParticulate mass corrected for blank value of 0.002 g.

^bQuotient of corrected total particulate mass collected and volume of gas sampled at actual conditions.

emissions from the process gas incinerator would amount to approximately 250 Mg (280 tons) per year.

Oxides of sulfur and nitrogen--Data from sampling of Geokinetics' gas streams for sulfur oxides (SO_x) and nitrogen oxides (NO_x), using EPA Methods 6 and 7, respectively, are presented in Tables 15 and 16. Sulfur oxides were detected in only one of the four samples taken upstream of the thermal incinerator at Retort No. 17, and that amount was insignificant, equivalent to less than one kilogram of emissions per day. Conversely, the average concentration of sulfur oxides in the incinerator exhaust was substantial (560 mg/m^3), resulting in emissions of 8.4 kg/hr to the atmosphere. Again extrapolating, sulfur dioxide emissions of $4,900 \text{ Mg}$ ($5,400 \text{ tons}$) annually are predicted for a retorting facility producing 320 m^3 of shale oil daily. The presence of sulfur oxides in the incinerator exhaust is due to combustion of sulfur compounds generated in the oil shale retorting process and hence contained in the process gas feed [3].

Nitrogen oxides were detected in all three gas streams sampled at Geokinetics Retort No. 17. The emissions of nitrogen oxides from the thermal incinerator, at a concentration of approximately 60 mg/m^3 for a mass flow rate of 0.9 kg/hr , are considerably less than those of sulfur oxides from the same source. Projected emissions from Geokinetics' proposed full-scale *in-situ* oil shale retorting operation are 530 Mg (580 tons) of nitrogen oxides per year, assuming all factors other than plant size remain the same. The data in Table 16 indicate that the nitrogen oxide content of the incinerator feed gas, that is, the demister outlet, makes only a minor contribution to the total. Based on information presented by Rolke [23], the amount of nitrogen oxides in the incinerator exhaust cannot be fully accounted for by the reaction of nitrogen and oxygen in the combustion air. Rolke's explanation that additional nitrogen oxides may be formed during incineration, when nitrogenous compounds such as ammonia are present in the feed stream [23], is indeed the case for Geokinetics' oil shale retorting technology, as discussed below.

Hydrocarbons--Samples from gas streams at Geokinetics Retort No. 17 were collected for determination of both total and specific hydrocarbon compounds. Analyses of Tedlar® bag samples for total hydrocarbons are reported as concentrations in Table 17 and as mass flow rates in Table 18. The concentration data for the demister inlet and outlet sample points exhibit very good reproducibility and, perhaps, the attainment of "steady-state" operations in Retort No. 17. On the other hand, the first sample

[23] Rolke, R. W., R. D. Hawthorne, C. R. Garbett, E. R. Slater, and T. T. Phillips. Afterburner Systems Study. EPA-R2-72-062, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, August 1972. 512 pp.

TABLE 15. QUANTIFICATION OF SULFUR OXIDES IN GAS STREAMS FROM GEOKINETICS RETORT NO. 17

Sample point	Concentration in gas stream (as SO ₂), ^a mg/m ³			Mass flow rate, kg/hr
	Run no. 1	Run no. 2	Average	
Demister inlet	0 ^b	18	9	0.02
Demister outlet	0 ^b	0 ^b	0	0
Incinerator outlet	640	470	560	8.4

^aConcentration in gas at actual conditions.

^bNot detected by analytical method used.

TABLE 16. QUANTIFICATION OF NITROGEN OXIDES IN GAS STREAMS FROM GEOKINETICS RETORT NO. 17

Sample point	Concentration in gas stream (as NO ₂), ^a mg/m ³			Mass flow rate, kg/hr
	Run no. 1	Run no. 2	Average	
Demister inlet	2.7	5.7	4.2	0.008
Demister outlet	4.0	4.0	4.0	0.006
Incinerator outlet	48	70	59	0.9

^aConcentration in gas at actual conditions.

TABLE 17. TOTAL HYDROCARBON ANALYSES OF GAS STREAMS FROM GEOKINETICS RETORT NO. 17

Sample point	Date and approximate sampling time	Number of replicate analyses ^a	Total hydrocarbon (THC) concentration (as CH ₄), ^b ppmv ^c		Average THC concentration (as CH ₄), ppmv
			1,050 ppmv CH ₄ std.	10,500 ppmv CH ₄ std.	
Demister inlet	7/19/79 12:30 PM	3	23,000	24,000	23,000
	7/19/79 3:00 PM	4	20,000	21,000	20,000
Demister outlet	7/20/79 10:00 AM	3	27,000	24,000	25,000
	7/20/79 4:00 PM	3	25,000	25,000	25,000
	7/21/79 1:30 PM	4	25,000	23,000	24,000
Incinerator outlet	7/21/79 10:30 AM	4	4,300	3,900	4,100
	7/21/79 3:30 PM	3	260	270	260
	7/21/79 4:30 PM	3	280	290	290

^a Multiple analyses of all samples were performed for calculation of total hydrocarbon concentration.

^b Determined from methane (CH₄) standards at the indicated concentrations.

^c Parts per million, by volume.

TABLE 18. MASS FLOW RATES OF TOTAL HYDROCARBONS IN GAS STREAMS FROM GEOKINETICS RETORT NO. 17

Sample point	Mass flow rate of total hydrocarbons (as CH ₄), ^a kg/hr
Demister inlet	19 ^b
Demister outlet	17 ^b
Incinerator outlet	10 ^c 0.6 ^d

^a Calculated using actual stack gas flow rates.

^b Based on average of total hydrocarbon concentrations from all samples taken, as shown in Table 22.

^c Based on: 1) total hydrocarbon concentration from sample taken on 7/21/79 at 10:30 AM, and 2) actual stack gas flow rate determined in Method 5 run conducted on 7/21/79 from 3:30 PM to 5:30 PM.

^d Based on: 1) average of total hydrocarbon concentrations from two samples taken on 7/21/79, one at 3:30 PM and one at 4:30 PM; and 2) actual stack gas flow rate determined in Method 5 run conducted on 7/21/79 from 3:30 PM to 5:30 PM.

taken from the incinerator outlet on July 21 appears to be spurious; a possible explanation is interference with incinerator operation due to concurrent work on the adjacent vacuum blower. Assuming the latter two incinerator exhaust samples are more representative, Table 18 indicates that the device accomplishes approximately 97 percent destruction of the hydrocarbons in the demister outlet gases. Residual hydrocarbon emissions of 0.6 kg/hr translate to 350 Mg (390 tons) released from a 320 m³ (2,000 bbl) per day shale oil production operation as planned by Geokinetics.

Selected Tedlar® bag samples described above were also analyzed for separate fractions of C₁ to C₆ hydrocarbons. Table 19 is a reduced form of the data which relates the fractions of higher hydrocarbons to the C₁ concentration data. For both the inlet and outlet of the mist eliminator for Geokinetics Retort No. 17, the amount of hydrocarbons present decreases monotonically with increasing molecular weight. In the case of the thermal incinerator, hydrocarbon quantities are approximately evenly distributed among the C₁ through C₅ fractions, with C₆ compounds present at slightly higher concentrations. These two observations would seem to indicate that the thermal incinerator's operating temperature is insufficient for oxidation of benzene derivations, such as toluene, which are relatively stable molecules [23]. This possibility is discussed further below.

The Tedlar® bag samples were also screened for specific organic compounds and classes of compounds using a Hewlett-Packard 5982A GC/MS system; the analysis results are given in Table 20. Compounds labelled "detected" produced readily identifiable peaks on a gas chromatograph scan, while those marked "trace" were identified by mass spectrometry but buried in the GC scans. Although benzene, toluene, and substituted benzenes were present in the demister inlet and outlet, none of these compounds were detected in the incinerator exhaust. This refutes the hypothesis made above regarding the performance of the thermal incinerator at Retort No. 17.

Porous polymer tubes packed with XAD-2 and Tenax resins were also used to sample specific hydrocarbon compounds and classes from Geokinetics gas streams. Table 21 lists the concentrations and mass flow rates of organic compounds collected by packed tubes; polynuclear aromatic hydrocarbons were not detected in any of the three samples. Of the materials detected, C₅ - C₁₀ aliphatic compounds were detected in the largest quantity, but then at concentrations less than 1 g/m³ and only in the demister inlet and outlet. The data of Table 21 again proves the effectiveness of thermal incineration as a means of controlling hydrocarbons in gas streams from *in-situ* oil shale retorting. Toluene, the only organic compound detected in the incinerator exhaust, was reduced by 80 to 95 percent relative to its amount in upstream sources.

TABLE 19. RELATIONSHIP OF HIGHER HYDROCARBONS TO C₁ HYDROCARBONS IN GAS STREAMS FROM GEOKINETICS RETORT NO. 17

Sample point	Date and approximate sampling time	Fraction of C ₁ concentration ^a				
		C ₂	C ₃	C ₄	C ₅	C ₆
Demister inlet	7/19/79 12:30 PM	0.22	0.09	0.07	0.04	<0.01
	7/19/79 3:00 PM	0.20	0.09	0.07	0.01	<0.01
Demister outlet	7/20/79 10:00 AM	0.42	0.16	0.11	0.06	<0.01
	7/20/79 4:00 PM	0.18	0.09	0.04	0.03	<0.01
Incinerator outlet	7/21/79 3:30 PM	1.1	0.81	0.66	1.9	5.4
	7/21/79 4:30 PM	0.85	0.58	0.47	1.2	4.5

^aEqual to quotient of C_x concentration to C₁ concentration.

TABLE 20. GC/MS ANALYSIS OF GEOKINETICS GAS STREAMS FOR SPECIFIC HYDROCARBONS (BAG SAMPLES)^a

Compound(s)	Sample point		
	Demister inlet	Demister outlet	Incinerator outlet
Benzene	D	D	ND
Toluene	T	T	ND
C ₃ - C ₁₀ Alkanes	D	D	ND
C ₄ - C ₆ Alkenes	D	D	ND
C ₂ Benzenes	T	T	ND
C ₁ - C ₃ Cyclohexanes	D	D	ND

^aD = detected; ND = not detected; T = trace.

Noncriteria Pollutants --

Ammonia--Ammonia was collected from the three gas stream sampling points at Geokinetics Retort No. 17 using a midjet impinger train with a sulfuric acid absorbing solution. Table 22 presents the relevant information quantifying ammonia emitted from the

TABLE 21. CONCENTRATIONS AND MASS FLOW RATES OF SPECIFIC HYDROCARBONS COLLECTED BY PACKED TUBES

Compound(s)	Concentration ^a and mass flow rate					
	Demister inlet		Demister outlet		Incinerator outlet	
	mg/m ³	kg/hr	mg/m ³	kg/hr	mg/m ³	kg/hr
Toluene	53	0.10	230	0.34	1 ^c	0.02
C ₅ - C ₁₀ Aliphatics ^b	470	0.89	880	1.3	-	-
C ₂ Benzenes	110	0.21	240	0.35	-	-
C ₃ Benzenes	62	0.12	110	0.16	-	-
C ₃ Cyclohexanes	110	0.21	240	0.34	-	-

^a Quotient of total mass of compound(s) collected, by both Tenax- and XAD-packed tubes, and volume of gas sampled at actual conditions.

^b This group includes straight-chain and branched alkanes, alkenes, and alkynes.

^c Not detected by analytical method used.

retort. The concentrations and mass flow rates of ammonia in the inlet and outlet of the mist eliminator are very similar to those for particulate matter at the same points (see Table 14). There was no ammonia detected in the incinerator exhaust, all that present in the feed gases having been combusted to nitrogen oxides as mentioned in the above discussion of the latter pollutant.

TABLE 22. QUANTIFICATION OF AMMONIA IN GAS STREAMS FROM GEOKINETICS RETORT NO. 17

Sample point	Ammonia collected (as NH ₃), mg	Concentration in gas stream, ^a mg/m ³	Mass flow rate, kg/hr
Demister inlet	34.0	1,100	2.0
Demister outlet	25.5	890	1.3
Incinerator outlet	0 ^b	0	0

^a Quotient of mass of ammonia collected and volume of gas sampled at actual conditions.

^b Not detected by analytical method used.

Arsine--Arsine (AsH_3), also known as arsenic trihydride or hydrogen arsenide, is a colorless, extremely poisonous gas with a disagreeable garlic odor. Table 23 presents the results of analyses for this specific arsenic compound in the inlet and outlet of the mist eliminator at Geokinetics Retort No. 17. Arsine was present only in minute concentrations, at or near the detection limit of the analytical method used.

TABLE 23. QUANTIFICATION OF ARSINE IN GAS STREAMS FROM GEOKINETICS RETORT NO. 17

Sample point	Sample number	Concentration in gas stream, ^a mg/m ³	Mass flow rate, kg/hr
Demister inlet	ID-1-AR	<0.005	$<6 \times 10^{-6}$
	ID-2-AR	0.005	6×10^{-6}
Demister outlet	OD-2-AR	0.009	13×10^{-6}

^aQuotient of mass of arsine collected and volume of gas sampled at actual conditions.

Hydrogen cyanide--A potassium hydroxide absorbing solution was used to sample hydrogen cyanide in process and stack gas streams at Geokinetics Retort No. 17. Table 24 lists the calculated concentrations and mass flow rates. The concentrations of hydrogen cyanide in the demister inlet and outlet gases were relatively low, and approximately equal to those of nitrogen oxides in similar samples. Table 24 indicates that more than 98 percent of the potential hydrogen cyanide emissions were removed by the thermal incinerator.

Trace elements--The particulate matter collected by the filters in the modified EPA Method 5 train and the contents of the corresponding impingers used to sample the process and stack gas streams from Geokinetics Retort No. 17 were analyzed for a total of 29 trace elements. Tables 25 and 26 present concentrations of trace elements present in the solid and vapor phases, respectively, at the sample gas temperatures. In determining these concentrations, corrected elemental masses, that is, the mass of the element measured in the sample minus the mass of the element in a blank, were used. The detection limits were determined while using distilled water and reference materials. Detection limits were not actually determined on wastewater samples. These limits should be considered instrument sensitivities. Due to the matrix of the sample, the actual detection limits could be considerably higher.

TABLE 24. QUANTIFICATION OF HYDROGEN CYANIDE IN GAS STREAMS FROM GEOKINETICS RETORT NO. 17

Sample point	Cyanide collected (as HCN), μg	Concentration in gas stream, ^a mg/m^3	Mass flow rate, kg/hr
Demister inlet	86	3.2	0.006
Demister outlet	99	4.3	0.006
Incinerator outlet	0.6	0.007	0.0001

^aQuotient of mass of cyanide collected and volume of gas sampled at actual conditions.

TABLE 25. CONCENTRATIONS OF TRACE ELEMENTS IN TOTAL PARTICULATE COLLECTED BY FILTERS

Element	Concentration, ^a $\mu\text{g}/\text{g}$	
	Demister inlet	Incinerator outlet
Arsenic	40	140 ^b
Boron	280	<1 ^b
Calcium	80	<0.04 ^b
Cobalt	2 ^c	10 ^c
Iron	50	<2 ^b
Lead	50 ^c	<23 ^b
Molybdenum	2 ^c	<11 ^b
Potassium	260	
Selenium	5	10
Sodium	720	<27 ^b
Tin	110	320

^aQuotients of corrected element mass and corrected total particulate mass collected by filters.

^bConcentration less than the indicated detection limit.

^cConcentration in analyzed sample was in the semi-quantitative range between the detection limit and the lowest quantitatively determinable concentration (LQDC).

TABLE 26. CONCENTRATIONS OF VOLATILE TRACE ELEMENTS
IN GASES SAMPLED BY IMPINGERS

Element	Concentration, ^a $\mu\text{g}/\text{m}^3$		
	Demister inlet	Demister outlet	Incinerator outlet
Antimony	2.1	2.8	4.0
Arsenic	130	38	0.4
Cadmium	1.0	1.2	0.9
Lead	18	10	20
Mercury	1.4	2.7	0.2
Selenium	-b	0.5	4.2

^aQuotient of total element mass and volume of dry gas sampled at standard conditions (20°C, 101.3 kPa).

^bSelenium, if present, was below the detection limit.

Boron, tin, iron, lead, and arsenic were the most significant trace elements detected in the particulate matter from the raw off-gases from Geokinetics Retort No. 17. Of these, tin and arsenic were present in the residual particulate emissions from the thermal incinerator, although only on the order of 0.01 percent. The apparent presence of calcium, potassium, and sodium in the particulates from the demister inlet gas is not meaningful, and is probably due to the variation in the composition of the filter material. Of the six "volatile" trace elements quantified in Table 26, arsenic is the one present at the greatest concentrations in the demister inlet and outlet gases, while lead is the only such material detected at a level greater than 10 $\mu\text{g}/\text{m}^3$ in the exhaust from the thermal incinerator. From information presented above, arsenic must exist in a form other than arsine in these gas samples from oil shale retorting.

Table 27 is an overall summary of the trace element emission data for Geokinetics Retort No. 17, listing the mass flow rates of each of 14 elements detected in one or more of the gas streams sampled. In the demister inlet gases, arsenic is the only element for which the mass flow rate of vaporous materials is greater than that from the particulate matter. In the exhaust from the thermal incinerator, the reverse is true for arsenic, and, relative to the mist eliminator inlet, the closure of the mass balance for arsenic is poor. The closure of the mass balance is satisfactory for antimony, cadmium, lead, and selenium, the only other elements for which particulate and vapor analyses were conducted in both the demister inlet and the incinerator outlet.

TABLE 27. MASS FLOW RATES OF DETECTABLE TRACE ELEMENTS IN GEOKINETICS GAS STREAMS

Element	Mass flow, ^a mg/hr					
	Demister inlet		Demister outlet ^b		Incinerator outlet	
	Particulate	Vapor	Particulate	Vapor	Particulate	Total ^c
Antimony	BDL ^d	2	2	2	BDL	10
Arsenic	80	150	230	30	60	60
Boron	560	- ^e	560	-	BDL	-
Cadmium	BDL	1	1	1	BDL	3
Calcium	160	-	160	-	BDL	-
Cobalt	4	-	4	-	4	-
Iron	100	-	100	-	BDL	-
Lead	100	20	120	8	BDL	70
Mercury	-	2	2	2	BDL	<1
Molybdenum	4	-	4	-	BDL	-
Potassium	520	-	520	-	BDL	-
Selenium	10	BDL	10	<1	4	20
Sodium	1,400	-	1,400	-	BDL	-
Tin	220	-	220	-	140	-

^aFor contribution from particulate, product of concentration (Table 25) and total particulate mass flow rate; for contribution from vapor, product of concentration (Table 26) and volumetric flow rate of dry gases at standard conditions.

^bParticulates in demister outlet were not analyzed for trace element content.

^cCombination of contributions from particulate and vapor.

^dBelow detection limit.

^eDash indicates analysis was not conducted for the element listed.

Bioassay Testing--

Materials submitted for bioassay testing by MRC and Litton Bionetics consisted of composites of filters and XAD-2 resin from two SASS train samples of the demister outlet gas from Geokinetics Retort No. 17. LASL was supplied with a composite retort water sample and the probe wash, condensate, and impinger water from one of the two runs. Of the three gas stream samples analyzed by LASL, only the impinger water exhibited bioactivity detected as point-mutation (TA-100)-inducing bacterial mutagens, at the relatively low level of 0.98 revertants per μL . No bacterial mutagens were detected in the absence of liver microsomal activation, indicating a lack of measurable direct-acting mutagenic compounds.

Filter sample--MRC obtained a weight loss of 3.4 grams upon Soxhlet extraction of the composite filter sample with acetone. Solvent exchange with dimethyl sulfoxide (DMSO) yielded the desired extract for testing, but also a small amount of insoluble material. In the Ames assay using Salmonella typhimurium strain TA-100, the soluble filter extract was not found to be toxic at concentrations up to 10 μL per plate, either with or without S-9 rat liver microsomal activation. Plate incorporation assays using strain TA-98 with microsomal activation demonstrated that the soluble filter extract was mutagenic, in a dose-response fashion, at concentrations from 0.2 to 10 μL per plate. Both the soluble and insoluble filter extracts were assayed in concentrated spot tests at 50 μL of sample per spot. With strain TA-98 and rat or mouse liver microsomal activation, the responses were similar, both samples yielding a slightly high number of revertants per plate. However, the mutagenic response was questionable because the revertants were not clustered; volatile materials may cause this type of general increase in the number per plate without a cluster of colonies being formed.

Upon Soxhlet extraction of the filter sample, Litton Bionetics obtained a very dark brown solution containing 4.04 grams of material at a concentration of 86.5 mg/mL [24]. Due to the difficulties experienced by MRC, LBI was instructed not to attempt solvent exchange with DMSO. The filter extract exhibited toxicity to Salmonella strains TA-98, TA-100, TA-1535, TA-1537, and TA-1538 at a 10 mg per plate dose level. In the absence of metabolic activation, the mutagenicity test results were positive with strain TA-1537; with activation, the SASS filter extract exhibited genetic activity with this strain and also with strains

[24] Jagannath, D. R., and B. C. Myhr. Evaluation of SASS Filter Extract from *In-Situ* Oil Shale Retorting in the Ames Mutagenicity, CHO Clonal Toxicity, and RAM Cytotoxicity Assays. Litton Bionetics, Inc., Kensington, Maryland, December 1979. 45 pp.

TA-98, TA-100, and TA-1538. Therefore, the acetone extract of the filter used to sample demister outlet gases from Geokinetics Retort No. 17 may be classified as having nondetectable toxicity and high mutagenicity.

Both MRC and LBI tested the SASS filter sample for clonal toxicity using Chinese hamster ovary cells (CHO-KI). The MRC assay results showed zero percent survival at a concentration of 1 μ L/mL and 16 percent survival at 0.5 μ L/mL, using the soluble filter extract. LBI's first trial showed that the test material had very little effect on CHO cell survival at concentrations from 0.03 to 100 μ g/mL. A second trial extended the assayed concentration range to 1,700 μ g/mL; the resulting data plot (Figure 13) yielded a median effective concentration (EC_{50}) of 165 μ g/mL [24]. Thus, the clonal toxicity of the SASS filter extract was evaluated as low, but approaching the region of moderate toxicity.

Litton Bionetics also determined the cytotoxicity of the SASS filter extract taken from the Geokinetics Retort No. 17 sample using rabbit alveolar macrophage (RAM) cells [24]. Acetone stock solutions at concentrations of 1 to 850 μ g/mL in the culture medium were tested. Five assay parameters were evaluated (viability, viability index, protein, adenosine triphosphate (ATP), and ATP per 10^6 cells), and all behaved similarly as a function of sample concentration. The EC_{50} value for culture ATP content, the most sensitive parameter, was 145 μ g/mL, indicating low toxicity of the test material.

Resin sample--MRC homogenized a portion of the composite XAD-2 resin sample, extracted the homogenate with acetone, and solvent-exchanged the test material with DMSO; no problems with solubility were encountered. At concentrations up to 10 μ L per plate, the XAD-2 resin extract was not mutagenic toward Salmonella in incorporation tests conducted with and without mammalian microsomal activation. Spot test assays at a concentration of 50 μ L of sample per spot also failed to indicate mutagenic activity toward any of the four bacterial strains, again either in the absence or presence of activation. In the toxicity assay, the resin extract was found not to be toxic to strain TA-100 at concentrations from 0.01 to 10 μ L per plate.

Litton Bionetics performed Soxhlet extraction of the XAD-2 resin sample, followed by concentration in a Kuderna-Danish evaporator [25]. In toxicity assays using the Ames method, the resin extract

[25] Jagannath, D. R., and B. C. Myhr. Evaluation of SASS XAD-2 Resin Extract from *In-Situ* Oil Shale Retorting in the Ames Mutagenicity CHO Clonal Toxicity, and RAM Cytotoxicity Assays. Litton Bionetics, Inc., Kensington, Maryland, December 1979. 45 pp.

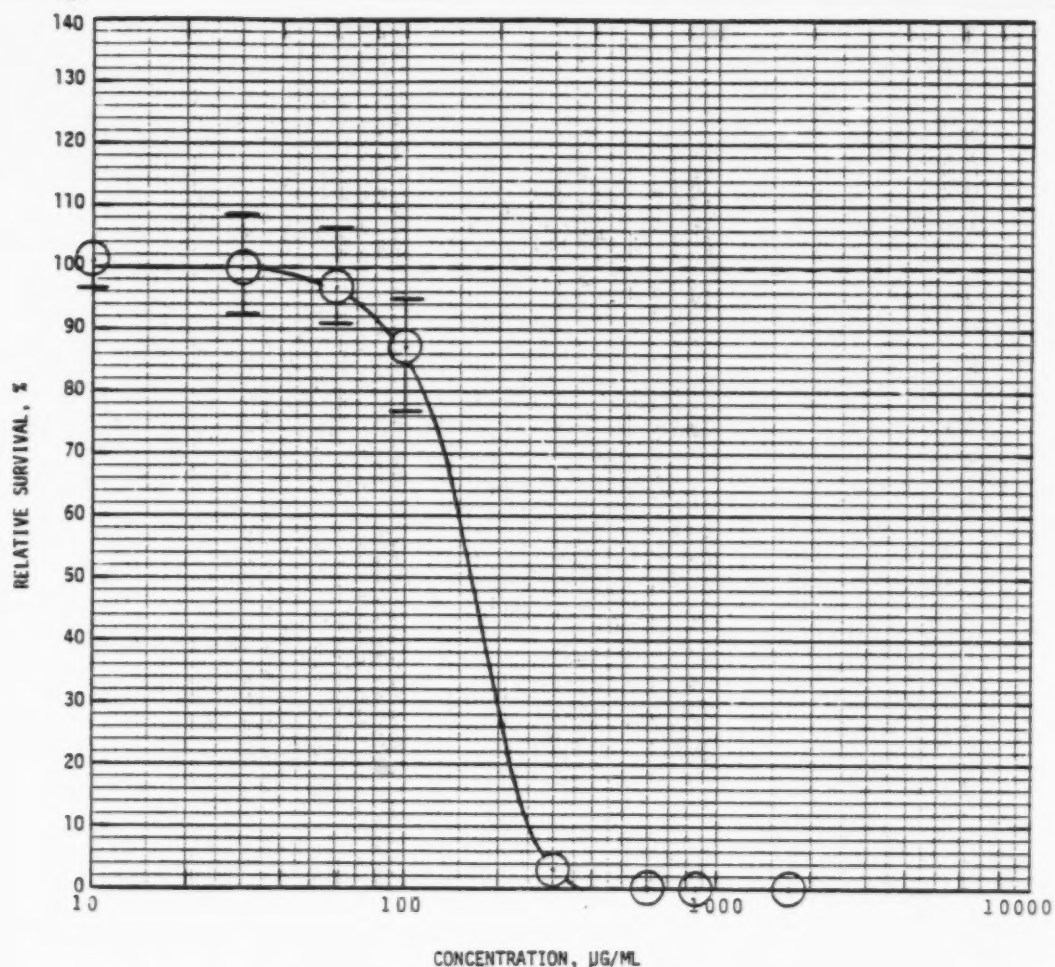


Figure 13. Results of CHO clonal toxicity assay of SASS filter extract [24].

was toxic to *Salmonella* strains TA-100, TA-1537, and TA-1538, and also to strain TA-98 in a repeat test, at a dose of 1.0 mg per plate. The test extract was toxic to all the above strains, and also to strain TA-1535, at 10 mg per plate. All mutagenicity tests of the XAD-2 resin extract were negative, whether or not rat liver microsomal activation was used. In summary, the toxicity of the extract of the SASS XAD-2 resin was classified as "low" and the mutagenicity as "not detectable." Note that comparison of these results with those for the filter sample indicates that the particulate matter extracted from the latter is the principal source of mutagenic activity in the outlet gases from the demister at Geokinetics Retort No. 17.

Clonal cytotoxicity assays of the XAD-2 resin sample using the CHO-KI cell line showed increased activity relative to that for the filter sample. In tests by MRC, total killing occurred at a concentration of 1 $\mu\text{L/mL}$, with six percent survival at 0.5 $\mu\text{L/mL}$. For comparison, percent survival at 0.5 $\mu\text{L/mL}$ was 16 percent for the filter sample and zero for the positive control (cadmium chloride). LBI conducted the cytotoxicity assay with stock solutions at concentrations from 0.1 to 700 $\mu\text{g/mL}$ [22]. The initial test sequence showed very little effect of the resin extract on CHO cell survival at concentrations up to 30 $\mu\text{g/mL}$, but complete lethality at 100 $\mu\text{g/mL}$ or higher. A second trial confirmed this response and located the EC_{50} value at 48 $\mu\text{g/mL}$ (see Figure 14). This classifies the XAD-2 resin extract as moderately toxic, that is, EC_{50} within the range of 10 to 100 $\mu\text{g/mL}$, compared to the low toxicity of the filter sample ($\text{EC}_{50} = 165 \mu\text{g/mL}$).

LBI also conducted RAM cytotoxicity assays of the SASS XAD-2 resin extract at dose levels from 1 $\mu\text{g/mL}$ to 700 $\mu\text{g/mL}$ [25]. Evaluation of all five assay parameters, previously listed, yielded EC_{50} values between 100 and 1,000 $\mu\text{g/mL}$. Therefore, the test material was classified as having low toxicity to the macrophage cells, as was also the case for the filter sample. For the cytotoxicity tests of the resin extract, the viability index and the ATP content of the culture were the most sensitive parameters, giving EC_{50} values of 130 $\mu\text{g/mL}$ and 145 $\mu\text{g/mL}$, respectively.

Fugitive Emissions

A specially designed collection system, described in Section 4, was utilized to sample fugitive gas emissions due to seepage through the overburden and from around instrumentation wells at Geokinetics Retort No. 17. Prior to transport to the field site, brass and stainless steel orifice meters for the sampling train were calibrated at the Dayton Laboratory using air. This information was needed to transform the observed pressure drop (ΔP_f) to an "effective pressure drop" (ΔP_e), using ratios of temperature and pressures at sampling and calibration conditions, as follows [26].

$$\Delta P_e = \Delta P_s \left(\frac{T_s}{T_c} \right) \left(\frac{P_c}{P_s} \right) \quad (1)$$

-
- [26] Patton, W. F., and J. A. Brink, Jr. New Equipment and Techniques for Sampling Chemical Process Gases (paper presented at the Air Pollution Control Association's 55th Annual Meeting, Chicago, Illinois, May 1962). 5 pp.

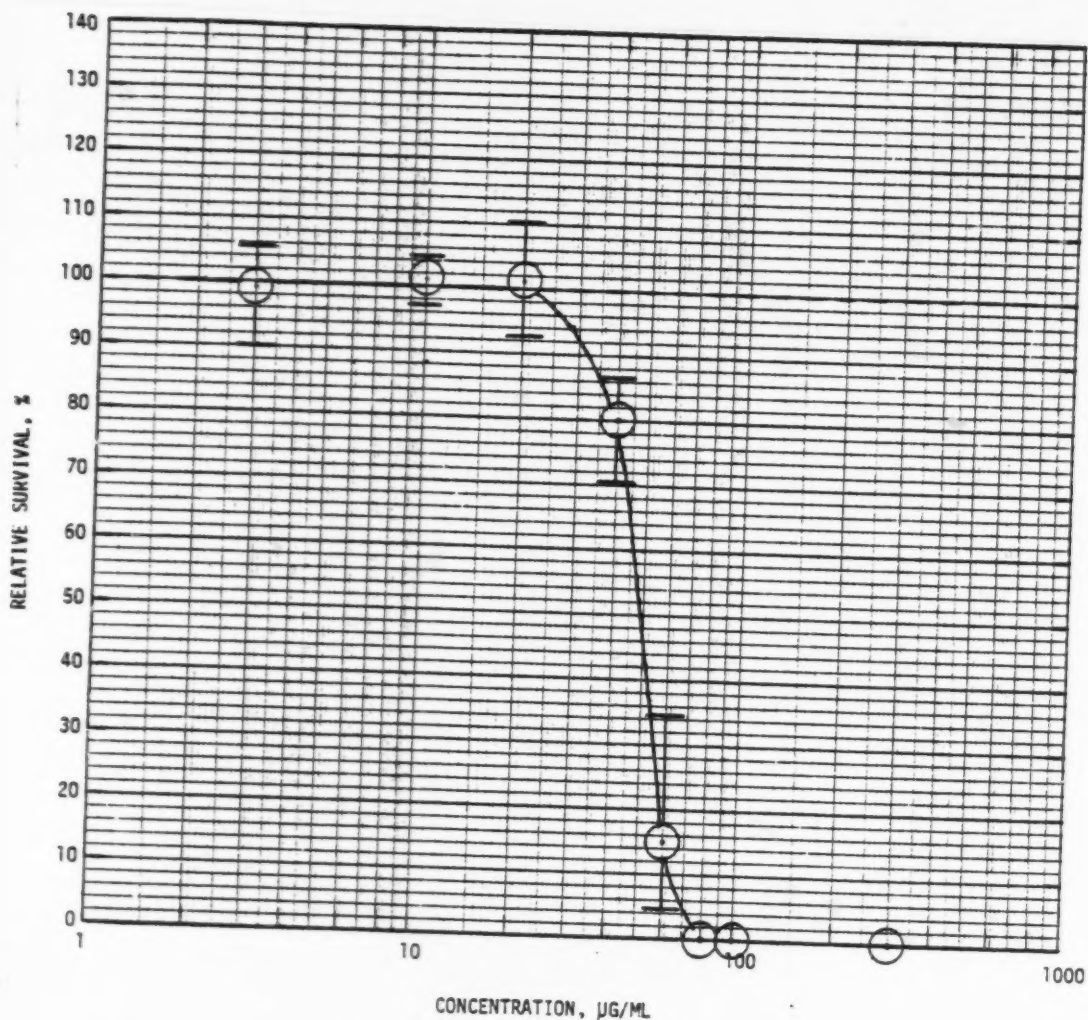


Figure 14. Results of CHO clonal toxicity assay of SASS XAD-2 resin extract [25].

where

- ΔP_e = "effective pressure drop", at calibration conditions, in H_2O
- ΔP_s = observed pressure drop, at sampling conditions, in H_2O
- T_s = temperature during sampling, $^{\circ}R$
- T_c = temperature during calibration, $^{\circ}R$
- P_c = barometric pressure during calibration, in Hg
- P_s = barometric pressure during sampling, in Hg

The corrected pressure drop was then used to determine the gas flow rate at calibration conditions from Table 28 or Figure 15.

TABLE 28. CALIBRATION DATA FOR FUGITIVE EMISSION SAMPLING TRAIN - STAINLESS STEEL ORIFICE^a

Pressure drop across orifice, in H ₂ O	Run time, min	Volume of gas, ft ³	Flow rate, ft ³ /min
0.25	11	5.20	0.47
0.40	8	5.35	0.67
0.50	8	5.51	0.69
0.60	9	6.75	0.75
0.75	7	5.76	0.82
1.0	9	8.36	0.93
1.5	5	5.44	1.09
2.0	5	6.12	1.22
2.5	5	6.73	1.35
3.0	5	7.20	1.44
4.0	4 ^b	6.38 ^b	1.60
4.5	- ^b	- ^b	2.07
5.0	- ^b	- ^b	2.13

^a Barometric pressure during calibration = 29.30 in Hg; temperature during calibration = 76°F = 536°R.

^b Data not available.

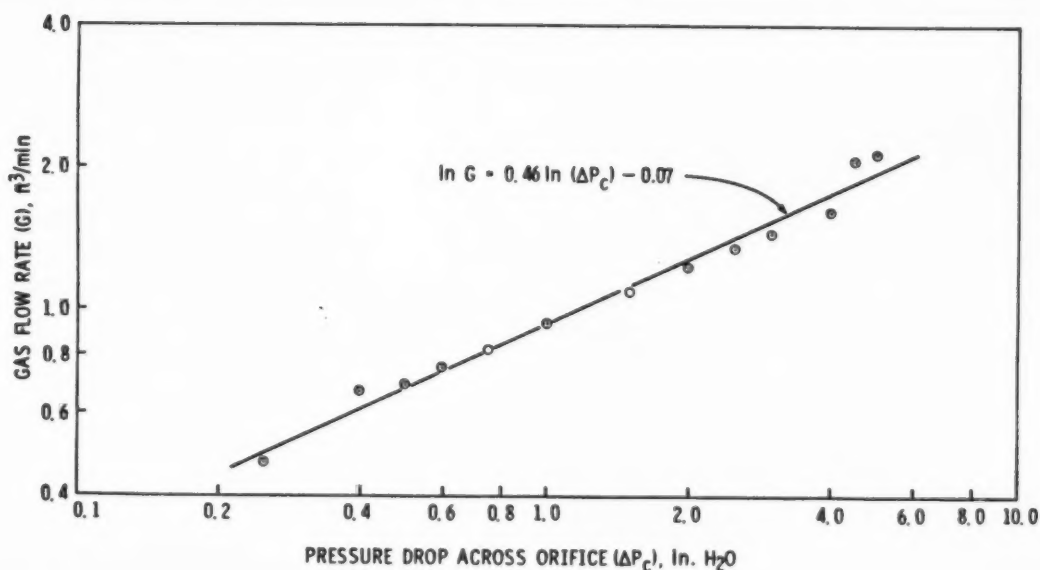


Figure 15. Calibration curve for stainless steel orifice (P = 29.30 in. Hg; T = 76°F).

This flow rate (G_C) was converted to sampling conditions, as follows:

$$G_S = G_C \left(\frac{T_S}{T_C} \right) \left(\frac{P_C}{P_S} \right) \quad (2)$$

where G_S = gas flow rate at sampling conditions, ft^3/min
 G_C = gas flow rate at calibration conditions, ft^3/min

The fugitive emission rate could then be calculated using Equation 3:

$$E = \frac{1.246 \times 10^{-3} M P_S G_S (C_S - C_b)}{T_S} \quad (3)$$

where E = fugitive emission rate, g/hr
 M = molecular weight of emitted material, g/g-mole
 C_S = concentration in sample, ppm
 C_b = concentration in field blank, ppm

The results of the above sequence of calculations for fugitive hydrocarbon emissions from Geokinetics Retort No. 17 are presented in Table 29. Emission rates from ground seepage samples, taken using the aluminum box described in Section 4, were normalized by division by the surface area of 0.37 m^2 . The average hydrocarbon emission rate for ground seepage was $5.5 \text{ g/m}^2/\text{hr}$, with a range of 0.2 to $18 \text{ g/m}^2/\text{hr}$. Figure 16 is a pictorial representation of the distribution of hydrocarbon emission rates over the surface of Retort No. 17, clearly showing that, on the average, emissions ahead of the burn front are greater than those behind it, as had been suggested by Geokinetics personnel.

Total fugitive hydrocarbon emissions from Retort No. 17 can be estimated as the product of the average ground seepage rate ($5.5 \text{ g/m}^2/\text{hr}$) and the retort surface area ($1,043 \text{ m}^2$) plus the product of the average emission rate from wells (5.3 g/hr) and the number of all types of wells (46); the resulting total emission rate is approximately 6.0 kg/hr . For comparison, the mass flow rate of vaporous hydrocarbons in the off-gas from Retort No. 17 was 17 to 19 kg/hr , only three times greater than the fugitive losses.

Another means by which to assess the impact of the fugitive hydrocarbon emissions from oil shale retorting is the use of dispersion modeling to calculate ambient air concentrations. Ground-level concentrations due to emissions from a ground-level

TABLE 29. FUGITIVE HYDROCARBON EMISSION RATES^a

Sample type and run number	Hydrocarbon emission rate g/m ² /hr	Sample type and run number	Hydrocarbon emission rate, g/m ² /hr
Ground seepage:		Ground seepage (continued):	
G-1	2.9	G-22	0.5
G-2	0.4	G-23	3.3
G-3	14	G-24	7.0
G-4	11	G-25	2.9
G-5	15	G-26	8.0
G-6	5.7	G-27	2.4
G-7	0.3		
G-8	0.7 ^b		
G-9	3.4	Liquid produc- well:	
G-10	6.8	P-1	7.8 ^b
G-11	18	Thermocouple wells: ^c	
G-12	10	T-1	- ^d
G-13	5.6	T-2	4.8 ^b
G-14	7.0	T-3	3.7 ^b
G-15	1.6	T-4	6.9 ^b
G-16	0.9	T-5	5.4 ^b
G-17	8.5	T-6	3.1 ^b
G-18	4.9		
G-19	2.4		
G-20	0.3		
G-21	0.2		

^a Calculated using Equation 3; emission rates per unit area determined by dividing hourly rate by sample box area of 0.37 m².

^b Emission rate given in g/hr (sample box not used).

^c Thermocouple well emission rates include contribution from ground area also enclosed during sampling.

^d Thermocouple well sample No. T-1 was not analyzed.

source, as in this case, can be calculated according to the method of Turner [27]:

$$X = \frac{0.6 Q}{\pi \sigma_y \sigma_z u} \exp \left[-\frac{1}{2} \left(\frac{y}{\sigma_y} \right)^2 \right] \quad (4)$$

[27] Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, May 1970. 84 pp.

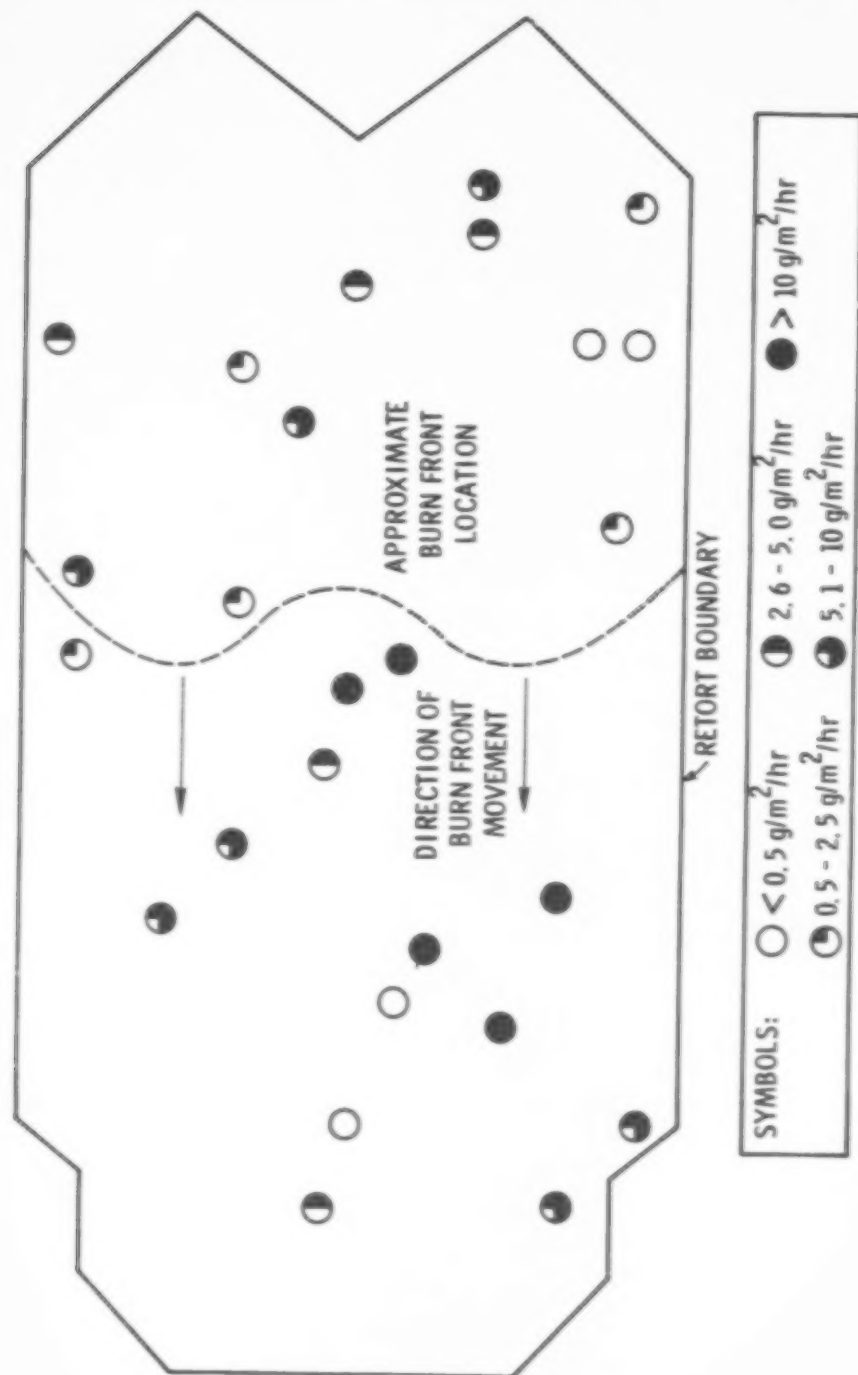


Figure 16. Pictorial representation of magnitude of fugitive hydrocarbon emissions due to seepage through retort surface.

where

- X = downwind ground-level concentration, g/m³
- Q = mass emission rate, g/s
- $\sigma_y = 0.2089 x^{0.9031}$
- $\sigma_z = 0.116 x^{0.905}$ for $x < 100\text{m}$
- $\sigma_z = 0.113 x^{0.911}$ for $x > 100\text{m}$
- x = downwind distance along the "plume" centerline, m
- y = horizontal distance from the "plume" centerline, m
- u = mean wind speed, m/s

These relationships assume that: 1) the emissions originate from a "point source", not strictly correct in this case but sufficient for order-of-magnitude estimation, 2) the atmosphere stability is represented by Class C, and 3) the averaging time is three hours, that for the ambient air quality standard for hydrocarbons. A wind speed of 3 m/s, equivalent to the national average but corrected from a height of 7 m to 1 m, was utilized in the calculations.

Table 30 is a matrix of downwind ground-level concentrations calculated using the total fugitive hydrocarbon emission rate of 1.66 grams per second from Geokinetics Retort No. 17. Assuming the "point source" of fugitive emissions is located at the midpoint of the downwind boundary of the retort, Table 30 indicates that, within a limited area nearby, the total hydrocarbon concentration exceeds the ambient air quality standard of 160 $\mu\text{g}/\text{m}^3$, although the latter includes only non-methane hydrocarbons. During the three-hour averaging time, this phenomenon occurs only within approximately 20 meters of the "plume" centerline and up to approximately 300 meters downwind of the retort. If annual average concentrations were calculated, the area exposed to hydrocarbon levels in excess of the standard would be even less, due to variation in wind direction. On the other hand, if extrapolated from a pilot-scale retort to a commercial facility operated at a much greater shale oil production rate, the effects of fugitive hydrocarbon emissions would extend to a larger area than that suggested by Table 30.

In addition to the quantification of fugitive hydrocarbon emissions from Retort No. 17, other analyses were conducted to determine their composition. Table 31 relates the presence of higher hydrocarbons to the C₁ fraction; as for the vented retort off-gases, lower-molecular-weight hydrocarbons dominate. Orsat analyses of selected fugitive emission samples are given in Table 32. Of most interest is the carbon monoxide emission rate, which for four of the five samples, is relatively large when compared to fugitive hydrocarbons. This may represent a potential health hazard to site personnel.

TABLE 30. DOWNWIND GROUND-LEVEL CONCENTRATIONS DUE TO FUGITIVE HYDROCARBON EMISSIONS FROM GEOKINETICS RETORT NO. 17

x, ^b meters	Concentration ^a , $\mu\text{g}/\text{m}^3$					
	y, ^c meters					
	0	10	20	50	100	200
10	69,000	- ^d	-	-	-	-
20	20,000	110	-	-	-	-
50	3,700	1,400	70	-	-	-
100	1,100	800	350	1	-	-
200	300	280	220	40	-	-
500	60	60	50	40	10	-
1,000	20	20	20	10	10	3
2,000	5	5	5	4	4	3

^aCalculated with Equation 4, using the total fugitive hydrocarbon emission rate of 1.66 g/s and dispersion data from Reference 27.

^bDownwind distance along the "plume" centerline.

^cHorizontal distance from the "plume" centerline.

^dDash indicates calculated concentration was less than $1 \mu\text{g}/\text{m}^3$.

WATER EFFLUENTS

Water samples were collected at two points associated with Geokinetics Retort No. 17. The "retort water" samples, which were light brown in color and at a temperature of about 40°C, were taken from a surge tank located downstream from the oil-water separator. The "evaporation pond water" samples, darker in color, were taken from a rubber-lined basin used to collect the overflow of wastewater from the surge tank mentioned above. The evaporation pond water represents a mixture of wastewaters generated by Geokinetics Retort No. 17 and all retorts previously burned at the Kamp Kerogen facility.

Water Quality Parameters and Conventional Pollutants

Table 33 lists the results of analyses of "water quality parameters" and "conventional pollutants" in both of the Geokinetics water samples. The analytical methods used were tested previously on a sample of Omega-9 oil shale retorting wastewater and found to give results which were generally reasonable, considering the scatter of the results reported by other laboratories.

As is typical of wastewaters from oil shale retorting, the total solids content of both the retort and evaporation pond water

TABLE 31. RELATIONSHIP OF HIGHER HYDROCARBONS TO C₁ HYDROCARBONS IN SELECTED FUGITIVE EMISSION SAMPLES

Sample type and run number	Fraction of C ₁ concentration ^a				
	C ₂	C ₃	C ₄	C ₅	C ₆
Ground seepage:					
G-4	0.21	0.06	0.01	0.03	<0.01
G-11	0.22	0.08	0.06	0.03	<0.01
G-14	0.27	0.08	0.06	0.02	<0.01
G-17	0.29	0.12	0.06	0.03	<0.01
G-24	0.28	0.09	0.09	0.04	<0.01
Liquid production well:					
P-1	0.33	0.12	0.06	0.02	<0.01
Thermocouple well:					
T-2	0.25	0.07	0.06	0.03	<0.01

^aEqual to quotient of C_x concentration to C₁ concentration.

TABLE 32. ORSAT ANALYSIS OF SELECTED FUGITIVE EMISSION SAMPLES

Sample type and run number	Concentration (dry basis), percent by volume			Carbon monoxide emission rate, ^a g/m ² /hr
	Carbon dioxide (CO ₂)	Oxygen (O ₂)	Carbon monoxide (CO)	
Ground seepage:				
G-9 ^b	0.2	10.6	1.0	21
G-13 ^c	5.0	7.0	1.1	23
G-18 ^b	4.0	7.2	0.8	17
G-24 ^b	8.0	5.8	0	0
Thermocouple well:				
T-4 ^c	3.6	7.4	1.8	40 ^d

^aCalculated using Equation 3.

^bConcentrations are averages of duplicate analyses of sample.

^cConcentrations are averages of triplicate analyses of sample.

^dEmission rate given in g/hr (sample box not used).

TABLE 33. WATER QUALITY PARAMETERS AND CONVENTIONAL POLLUTANTS IN GEOKINETICS SAMPLES

Component	Concentration, mg/L ^a	
	Retort water	Evaporation pond water
Alkalinity (as CaCO ₃)	16,600	22,400
Biological oxygen demand (BOD)	2,000	^b
Chemical oxygen demand (COD)	7,240	10,900
Conductivity ^c	11,200	20,000
Hardness (as CaCO ₃)	33.9	123 6
Oil and grease	186	648
pH	8.9	8.9
Solids, total ^e	1.02	2.91
Solids, total dissolved ^e	0.94	2.84
Solids, total volatile	0.19 ^f	0.43
Solids, total volatile dissolved ^e	0.21 ^f	0.40
Total inorganic carbon	1,100	2,200
Total organic carbon (TOC)	2,150	2,900
Bicarbonate (as HCO ₃ ⁻) ^g	5,380	10,800
Carbonate (as CO ₃ ⁼) ^g	178	345
Chloride	1,100	3,330
Cyanide (as CN ⁻)	95	266
Fluoride	15.6	41.6
Nitrogen, ammonia ^h	870	1,200
Nitrogen, ammonium ^{h, i}	317	437
Nitrogen, Kjeldahl ^h	1,230	1,250
Nitrogen, nitrate ^h	9,500	20,000
Nitrogen, nitrite ^h	0.083	0.067
Nitrogen, organic ^h	355	50
Orthophosphate (as P)	1.30	1.77
Phenolics	37.8	24.0
Phosphorus (as P)	4.30	1.77
Sulfur, total (as S)	1,230	4,170
Sulfate (as SO ₄ ⁼)	825.0	3,075.0
Sulfide (as S ⁼)	0.214	1.14
Sulfite (as SO ₃ ⁼)	400	1,150
Tetrathionate (as S ₄ O ₆ ⁼) ^j	1,080	3,700
Thiocyanate (as SCN ⁻)	325	1,025
Thiosulfate (as S ₂ O ₃ ⁼)	<25	<25

^a Except as noted.

^b Insufficient amount of sample to perform analysis.

^c $\mu\text{mhos/cm}$

^d Dimensionless

^e Percent (%)

^f All of the volatile solids in the retort water sample are dissolved.

^g Calculated from the inorganic carbon analysis.

^h Reported as elemental nitrogen (N).

ⁱ Ammonium nitrogen was calculated after analyses for other nitrogen compounds.

^j Cyanolysis and spectrophotometric estimation of tetrathionate in mixture with thiosulfate and tetrathionate (Analytical Chemistry, 41:898, 1969).

samples are high, 1.0 percent and 2.9 percent, respectively. Almost all of the solids were soluble, dissolved solids accounting for 92 percent of the total in the retort water sample and 98 percent in the evaporation pond water. Both samples were shown to be moderately alkaline, with a pH of 8.9. Both samples have relatively large chemical oxygen demands (retort water: 7,200 mg/L; evaporation pond water: 10,900 mg/L), which is also indicated by the total carbon concentrations.

Organic Priority Pollutants

The water samples from Geokinetics Retort No. 17 were also analyzed for 89 organic priority pollutants, excluding pesticides and polychlorinated biphenyls. The laboratory results are summarized in Table 34, which includes the analysis of a "method blank" using organic-free water. Ten of the priority pollutants were present in the retort water at concentrations greater than those for the method blank, whereas the evaporation pond water sample contained 17 of the compounds.

Phenol (670 µg/L), benzene (370 µg/L), toluene (280 µg/L), and acrylonitrile (250 µg/L) were the priority pollutants present in the largest concentrations in the retort water sample. None of these priority pollutants appear to be cause for concern because the concentrations do not exceed 1 ppm. The retort water sample also contained trace quantities (<10 µg/L) of polynuclear aromatic compounds (acenaphthylene, anthracene, and phenanthrene) and chlorinated hydrocarbons (methylene chloride, tetrachloroethylene, and trichloroethylene). Within the screening protocol, the analytical methods employed are semiquantitative at best, and the reported values may vary by a factor of two to ten.

The major priority pollutants observed in the evaporation pond water sample were acrylonitrile (1,700 µg/L), acrolein (360 µg/L), and phenol (230 µg/L). In addition to the three polynuclear aromatic compounds detected in the retort water sample, the pond sample contained chrysene, fluoranthene, and pyrene, again all at concentrations less than 10 µg/L. The evaporation pond water contained 1.7 ppm of acrylonitrile, approximately seven times its concentration in the retort water, as well as very much smaller quantities of di-n-butyl and di-n-octyl phthalates.

Comparison of the priority pollutant concentrations in the two Geokinetics water samples shows that amounts in the evaporation pond are greater than those in the retort water except for benzene, ethylbenzene, phenol, and toluene. Relative to that of water, the boiling points of the last three compounds are higher, whereas that of benzene is lower; this seems to eliminate volatilization as an explanation.

TABLE 34. ORGANIC PRIORITY POLLUTANTS IN GEOKINETICS SAMPLES^a

Compound	Concentration, µg/L		
	Retort water	Evaporation pond water	Method blank
Acids:			
Phenol	670	230	_b
Base/Neutrals:			
Acenaphthylene	11	92	-
Anthracene and phenanthrene	3.6	10	1.3
Bis(2-ethylhexyl) phthalate	0.5	3.8	9.0
Butyl benzyl phthalate	-	-	0.5
Chrysene	-	0.9	-
Di-n-butyl phthalate	-	0.8	0.6
Diethyl phthalate	-	3.5	13
Dimethyl phthalate	-	-	1.8
Di-n-octyl phthalate	-	1.5	0.6
Fluoranthene	-	8.3	-
Fluorene	-	-	0.4
Pyrene	-	3.2	-
Direct Injectables:			
Acrolein	-	360	-
Acrylonitrile	250	1,700	-
Volatiles:			
Benzene	370	67	0.5
Chloroform	-	2.0	-
Ethylbenzene	45	29	0.2
Methylene chloride	11	22	0.8
Tetrachloroethylene	0.9	0.5	-
Toluene	280	64	3.6
Trichloroethylene	1.7	2.8	1.4

^aCompounds not listed here, if present, were at concentrations below detection limits.

^bDash indicates that, if present, compound is at a concentration below its detection limit.

Trace Elements

Retort water and evaporation pond water for Geokinetics Retort No. 17 were analyzed for 30 trace elements (Table 35 lists the results). The higher concentrations of the alkali metals (calcium, magnesium, potassium, sodium) are probably due to the dissolved and suspended solids present in both samples. Of more interest are the relatively large amounts of boron (61 to 186 ppm) and arsenic (2 to 15 ppm) detected in both the retort water and the

TABLE 35. CONCENTRATIONS OF TRACE ELEMENTS
IN GEOKINETICS WATER SAMPLES^a

Element	Concentration, µg/L	
	Retort water	Evaporation pond water
Aluminum	350	510
Antimony ^b	110	440
Arsenic ^b	1,600	15,000
Barium	220	370
Beryllium	- ^c	- ^c
Boron	61,000	186,000
Cadmium	20	20
Calcium	6,600	11,000
Chromium	40	60
Cobalt	110	250
Copper	40	70
Iron	800	1,600
Lead	140	200
Magnesium	8,900	31,000
Manganese ^b	10	30
Mercury ^b	40	30
Molybdenum	270	6,900
Nickel	490	760
Phosphorus	740	1,500
Potassium ^b	29,000	57,000
Selenium ^b	20	280
Silicon	310	960
Silver	50	130
Sodium	0.28 ^d	0.83 ^d
Strontium ^b	690	890
Thallium ^b	- ^c	- ^c
Tin	50 ^e	100
Titanium	20	40
Vanadium	120	300
Zinc	60	100

^aAnalyses by inductively coupled argon plasma optical emission spectroscopy except as noted.

^bAnalysis by atomic absorption.

^cBelow detection limit.

^dPercent (%).

^eConcentration is in semi-quantitative range between detection limit and LQDC.

evaporation pond water. The presence of so much arsenic seems to rule out the possibility of biological activity in the evaporation pond, which might have explained the anomaly in the relative concentrations of benzene-based compounds in the two samples. Both the retort water and the evaporation pond water contained iron, phosphorus, and strontium at concentrations greater than 0.5 ppm, which is significant when compared to those for most of the metals analyzed. In addition, the evaporation pond sample contained nearly 7 ppm of molybdenum, representing a concentration factor of about 25 relative to the retort water.

Bioassay Testing

LASL tested the retort water for mutagenicity using the Salmonella typhimurium assay at doses from 0.2 to 400 μ L per plate. With rat liver microsomal activation, both frame-shift (TA-98)- and point-mutation (TA-100)-inducing bacterial mutagens were observed, at levels of 0.54 and 0.90 revertants per plate, respectively. LASL personnel considered this degree of bioactivity to be low, almost negligible.

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